UNIVERSIDAD COMPLUTENSE DE MADRID

FACULTAD DE CIENCIAS QUÍMICAS

Departamento de Ingeniería Química

TESIS DOCTORAL

Remediación de suelos con fases líquidas no acuosas mediante oxidación química in situ

MEMORIA PARA OPTAR AL GRADO DE DOCTOR

PRESENTADA POR

Fernando Pardo Pardo

Directores

Arturo Romero Salvador
Aurora Santos López

Madrid, 2017

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REMEDIACIÓN DE SUELOS CON FASES LÍQUIDAS NO ACUOSAS MEDIANTE OXIDACIÓN QUÍMICA IN SITU /
REMEDIATION OF SOILS WITH NON-AQUEOUS PHASE LIQUIDS BY IN SITU CHEMICAL OXIDATION

MEMORIA

que para optar al Grado de Doctor con mención europea por la Universidad Complutense de Madrid en el Programa de Doctorado en Ingeniería Química presenta

Fernando Pardo Pardo

Madrid, 2016

El Dr. Arturo Romero y la Dra. Aurora Santos López, catedráticos de Ingeniería Química, afirman haber dirigido el trabajo recogido en la presente memoria titulada "Remediación de suelos con fases líquidas no acuosas mediante Oxidación Química in Situ" que ha sido realizado en el Departamento de Ingeniería Química de la Facultad de Ciencias Químicas de la Universidad Complutense de Madrid, siendo subvencionado por varios proyectos concedidos por instituciones públicas, y que, a su juicio, reúne los requisitos de originalidad y rigor científico necesarios para ser presentada como Tesis Doctoral.

Madrid, _ de _ de _

Vº. Bº. de los Directores de la Tesis

Prof. Dr. Arturo Romero Salvador Prof. Dra. Aurora Santos López

Fernando Pardo Pardo

A todos aquellos que, a lo largo de
estos años, me preguntaron
inocente, cariñosa e
impacientemente "¿Cuándo lees la
tesis?". Y en especial, a mis padres
y a mi hermano

Agradecimientos

En primer lugar, quiero mostrar mi más sincero agradecimiento al Dr. Arturo Romero y a la Dra. Aurora Santos por la oportunidad que me dieron para realizar la tesis doctoral en su grupo de investigación, y sobre todo por su tiempo, paciencia y dedicación a la hora de dirigirla. Sin su ejemplo en el día a día, consejos y recomendaciones no hubiese sido posible realizar este trabajo.

También quiero agradecer enormemente la ayuda de la Dra. Juana María Rosas por compartir su tiempo y conocimientos conmigo en los primeros años de la tesis, que me resultaron de inestimable valía para aprender a desenvolverme en el mundo de la remediación de suelos, desde el trabajo diario en el laboratorio hasta la posterior publicación de los artículos.

Ao grupo de Engenharia Biológica da Universidade do Minho, especialmente á Prof. Teresa Tavares por ter me dado a oportunidade de trabalhar e aprender novos conhecimentos envolvidos na remediação dos solos. Também não me esqueço de Filomena, Bruna, Cassia e Dulu, do grupo BRIDGE.

Agradezco también el apoyo, la experiencia compartida por el personal técnico del laboratorio, en especial a Inma, Jose, al personal del taller de vidrio y al personal técnico del laboratorio de Química Física.

Quiero hacer mención especial a Ernesto, Sergio, Carlos y Loren por haberme dado la oportunidad, no solo de haber aprendido mucho de ellos codo con codo en el laboratorio, sino por esos momentos de pajareo y de buen rollo que solo pueden tener los grandes amigos.

Estoy también muy agradecido a la gente del laboratorio que estuvo conmigo al comienzo, como Fervi, Mari Pili, Pilar, Elena y Ángel, cuyo afecto y buena compañía me hicieron sentir como uno más del grupo nada más llegar.

A toda esa gente, que en periodos cortos, ya bien por estancias breves, proyectos fin de carrera o trabajos fin de master me hicieron la vida mucho más fácil con el desarrollo experimental y con la convivencia. Por ello no me puedo olvidar de Marina, Luque, Pau, Dani, Joana, Diana, Nikoletta, Remy, Lía, Virginia, María, Noelia, Vanesa, Joana y Eva.

A los que llegaron en el último momento, pero por ello no menos importante, y que con su calidad humana e inestimable compañía en el laboratorio me han soportado en los últimos compases del doctorado. Muchas gracias Miguel, Carmen y Lucía.

A todos los antiguos compañeros de la carrera y a los amigos de Coslada, Aldea, Santander, Braga, Nápoles, Cracovia, con lo que he compartido inolvidables momentos todo este tiempo y espero seguir compartiéndolos.

A Antía, que no sé cómo me aguanta, pero me aguanta, le daré siempre las gracias por su cariño y apoyo incondicional.

Y por supuesto, a mis padres y a mi hermano. Muchas gracias por todo, porque sin vosotros esta meta habría sido realmente inalcanzable.

Muchismas Gracias!!!

"El modo de dar una vez en el clavo es dar cien veces en la herradura"

Miguel de Unamuno (hace mucho tiempo).

Este trabajo fue realizado gracias a la concesión de una beca del programa Nacional de Formación de Personal Investigador (FPI) por el Ministerio de Economía y Competitividad (BES2011-044329), y con financiación del Plan Nacional de I+D+i del Ministerio de Ciencia e Innovación a través del proyecto de investigación CTM2010-16693, y del Ministerio de Economía y Competitividad a través del proyecto CTM2013-43794-R así como de los proyectos de investigación del grupo CARESOIL (S2009AMB-1648 y S2013MAE-2739) por parte de la Comunidad Autónoma de Madrid. Sin estas financiaciones no habría sido posible realizar esta Tesis Doctoral.

Septiembre de 2016

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RESUMEN
SUMMARY

RESUMEN

El aumento de la conciencia medioambiental a nivel global en las últimas décadas ha permitido mejorar el nivel de conocimiento en una gran variedad de campos relacionados con la conservación del medioambiente, destacando entre ellos los que centran sus estudios en torno a la contaminación de suelos por contaminantes de naturaleza orgánica. Asimismo, se han conseguido avances importantes en relación al estudio del comportamiento de los contaminantes presentes en el suelo, tanto de sus efectos y consecuencias sobre el medioambiente y la salud humana, como del desarrollo de medidas eficientes para su recuperación. A su vez, es importante tener en cuenta que todo este progreso no podría haber sido posible sin la creación de un marco legal capaz de identificar eficientemente las grandes dimensiones del problema, desde el estudio de riesgos hasta la búsqueda de responsabilidades con objeto de poner en marcha estrategias útiles para recuperar los espacios contaminados. En este sentido, en un gran número de países se han ido desarrollando los respectivos marcos legales con este propósito, como es el caso de Estados Unidos (EPA), Unión Europea, Australia y Canadá, entre otros.

Aunque la variedad de contaminantes orgánicos de distinta naturaleza que pueden estar presentes en un suelo es muy grande, hay ciertas propiedades comunes a los contaminantes más persistentes, como son una baja o nula solubilidad en agua, alta hidrofobicidad, alta afinidad con la materia orgánica del suelo, baja volatilidad y baja biodegradabilidad. Dado que el número y circunstancias en las que se pueden encontrar los contaminantes en el suelo son muy variados, también lo son las posibilidades y diversas técnicas que pueden llevarse a cabo para la remediación de suelos contaminados. En el abanico de posibilidades a la hora de seleccionar una técnica de remediación, cabría destacar aquellas técnicas basadas en la oxidación química in situ de los contaminantes (en inglés ISCO). El interés creciente en la aplicación y desarrollo de este tipo de técnicas se ha debido principalmente a su prometedor futuro como alternativa eficiente a las técnicas tradicionales de remediación de suelos, como son el *bioventing, air sparging y pump-and-treat*.

Teniendo en cuenta que las técnicas de oxidación química In Situ se fundamentan en la liberación de radicales con elevado poder de oxidación, como es el caso de los

radicales hidroxilo en el reactivo Fenton (E = 2.8 V) y los radicales sulfato (E = 2.6 V) en el uso de persulfato activado, su aplicación puede llegar a alcanzar elevadas eficiencias de eliminación de los contaminantes, incluso pudiendo llegar a conversión casi completa, además de buenos grados de mineralización en plazos de tiempo relativamente cortos. Estas ventajas que ofrece la oxidación química In Situ han ayudado a que el número de estudios sobre la aplicación de reactivo Fenton y persulfato activado hayan ido en aumento a lo largo de los años, desarrollándose a su vez formas cada vez más eficientes de oxidación química sobre suelos contaminados reales.

Es, por tanto, en este contexto en el que se ha enmarcado el desarrollo de la presente tesis doctoral, que ha estado centrada en el estudio de diferentes alternativas de aplicar el reactivo Fenton y persulfato activado para la eliminación de varios contaminantes orgánicos (gasolinas, mezcla de biodiesel e hidrocarburos aromáticos policíclicos). El trabajo se ha fundamentado en el estudio de la influencia de diversas variables, como tipo de catalizador, tipo de activador, concentración de activador/catalizador, concentración de oxidante, carga contaminante, etc., en la eliminación de los contaminantes tras los tratamientos, así como de la monitorización de cada una de las variables críticas involucradas en la evolución del tratamiento, como concentraciones de oxidante y contaminante remanentes, concentración de catalizador/activador, pH, concentración de agente quelante, etc… permitiendo así profundizar en la comprensión de los fenómenos subyacentes a la técnica de remediación durante su aplicación..

Los estudios realizados en la tesis se han llevado a cabo aplicando las técnicas de oxidación química In Situ en la remediación de un suelo franco arenoso contaminado artificialmente por distintos tipos de contaminantes a diferentes concentraciones. La selección de los contaminantes se ha realizado teniendo en cuenta un orden de solubilidad en agua decreciente. Se comenzó con etilbenceno, se continuó con una mezcla de diesel y biodiesel B20 y se finalizó con hidrocarburos aromáticos policíclicos. Cabe destacar que el desarrollo experimental así como el análisis y estudio de los resultados correspondientes aparecen publicados de manera detallada en artículos de revistas indexadas en el campo de la ingeniería química / medioambiental. Es por ello que la presente tesis contribuye a la expansión del conocimiento en el campo de la remediación medioambiental por técnicas de oxidación química, especialmente aquellas basadas en el uso del reactivo Fenton y persulfato activado para la eliminación de

contaminantes orgánicos persistentes en suelos. A continuación se resumen los bloques en los que se ha organizado la presente tesis doctoral:

i. Etilbenceno como contaminante representativo de gasolinas

- **Uso del reactivo Fenton modificado en discontinuo (Pardo et al., 2015b):** El objeto del tratamiento fue un suelo contaminado con etilbenceno, uno de los compuestos más persistentes en suelos del grupo de los BTEX, que se encuentra habitualmente en suelos que han estado expuestos a gasolina durante un largo periodo de tiempo debido a su menor volatilidad que el resto de BTEX y facilidad de interactuar con la materia orgánica del suelo. En este sentido, el artículo "*Remediation of soil contaminated by NAPLs using modified Fenton reagent: application to gasoline type compounds.*" Pardo F, Rosas JM, Santos A, Romero A. Publicado en la revista *Journal of Chemical Technology and Biotechnology* 2015; 90: 754-764, recoge detalladamente el desarrollo experimental y los resultados correspondientes a la aplicación del reactivo Fenton modificado para la eliminación de etilbenceno. Como agente quelante se utilizó citrato de sodio tribásico y los experimentos se llevaron a cabo en condiciones circumneutrales sin ajuste de pH. Se estudió el efecto de la dosis de oxidante, dosis de catalizador, en forma de ión férrico (Fe(III)), y la concentración de contaminante en el suelo, sobre la eficiencia de eliminación de etilbenceno tras el tratamiento. Además se realizó un seguimiento, durante el transcurso de la reacción, de variables clave involucradas en el proceso como pH, concentración de quelante, concentración de Fe(III), concentración remanente de oxidante y contaminante. Atendiendo a los resultados, se obtuvieron mayores eficiencias de eliminación cuando se trabajó con las mayores relaciones molares de oxidante/contaminante. Sin embargo, también se observó que, como resultado de una limitación al transporte de materia entre fases, la solubilidad del etilbenceno limitaba su concentración máxima en la fase acuosa. Además, dado el papel del etilbenceno como secuestrador de radicales en la fase acuosa, se produjo un consumo más lento, tanto de oxidante como de agente quelante cuando la concentración de contaminante se aumentó.

ii. Componentes de - biodiesel B20 (20% ésteres metílicos de ácidos grasos (FAME) y 80% de hidrocarburos procedentes del diesel convencional, principalmente alifáticos)

- **Uso del reactivo Fenton modificado en discontinuo (Pardo et al., 2014):** Con objeto de estudiar la efectividad del reactivo Fenton modificado hacia contaminantes más persistentes que los componentes de gasolinas, se utilizó un suelo contaminado con una mezcla de biodiesel B20 (20% ésteres metílicos de ácidos grasos y 80% componentes diésel fósil). El trabajo queda recogido en la publicación *"Remediation of a biodiesel blend-contaminated soil by using a modified Fenton process*." 2014; 21: 12198-12207. Pardo F, Rosas JM, Santos A, Romero A. Publicada en la revista *Environmental Science and Pollution Research*. Dados los buenos resultados obtenidos en la eliminación de etilbenceno, se utilizó el reactivo Fenton modificado para evaluar su eficacia hacia - biodiesel B20. En este trabajo, el objetivo principal se centró en el estudio de la eficiencia de eliminación de dos tipos de contaminantes presentes en un mismo combustible, biodiesel de tipo B20, con 20% de biodiesel en forma de ésteres metílicos de ácidos grasos y un 80% de diesel convencional, constituido principalmente por hidrocarburos alifáticos. Los experimentos de remediación se llevaron a cabo bajo diferentes condiciones, modificando la dosis de oxidante y de catalizador, la concentración de contaminante y la presencia de agente quelante. Asimismo, se observó que las condiciones experimentales que llevaron a mejores eficiencias de eliminación no implicaronn adición de quelante y cuando las concentraciones de oxidante y catalizador fueron mayores, se obtuvieron las mejores conversiones de contaminante. El citrato de sodio no mejoró la eliminación del contaminante siendo su oxidación mayor que la degradación del propio contaminante. Por último, se alcanzaron eficiencias de eliminación altas para los FAME, mientras que para los componentes alifáticos del diesel hubo una resistencia mucho mayor a la degradación.

- **Uso de persulfato activado en discontinuo (Pardo et al., 2015a):** Los mejores resultados con el tratamiento de reactivo Fenton modificado se dieron bajo condiciones en las que se daba un consumo muy rápido de oxidante y una

acidificación importante del medio, este tipo de circunstancias se traducen en que la aplicación de esta técnica en casos reales sea poco atractiva, dadas las dificultades que podría conllevar el transporte de los reactivos a la zona contaminada como consecuencia del elevado consumo improductivo de oxidante. Por tanto, la necesidad de buscar una alternativa eficiente y factible que implicase buena eficiencia de eliminación de contaminantes así como una buena estabilidad del agente oxidante en suelo llevó al estudio de la remediación de un suelo contaminado con - biodiesel B20 utilizando persulfato activado. El estudio se publicó con el título *"Remediation of a Biodiesel Blend-Contaminated Soil with Activated Persulfate by Different Sources of Iron."* 2015; 226: 17. Pardo F, Rosas JM, Santos A, Romero A. en la revista *Water Air and Soil Pollution*. En este trabajo se probaron diferentes maneras de activar el persulfato: ión ferroso (Fe(II)) quelado con citrato de sodio, Fe (II), partículas granulares de hierro cero-valente (gZVI) y nanopartículas de hierro cero-valente (nZVI). En la activación con hierro quelado se observó que el agente quelante se degradó mucho más que el propio contaminante, como ya había sucedido para el reactivo Fenton. Por otro lado, la mayor eficiencia de eliminación se alcanzó con la activación de nZVI gracias a su acción como fuente continua de hierro, minimizando el consumo improductivo de oxidante. En cuanto al tipo de contaminantes eliminados, se observó, de manera análoga al anterior tratamiento, que los hidrocarburos alifáticos procedentes del diésel convencional fueron mucho más resistentes a la oxidación que los FAME.

iii. <u>Hidrocarburos aromáticos policíclicos (PAH)</u>

- **Reactivo Fenton en discontinuo (Pardo et al., 2016a):** Se estudió la aplicación del reactivo Fenton sobre la eliminación de ciertos PAH. El estudio "*Optimization of the application of the Fenton chemistry for the remediation of a contaminated soil with polycyclic aromatic hydrocarbons."*. 2016, 91. 1763-1772. Pardo F, Peluffo M, Santos A, Romero A. publicado *online* en la revista *Journal of Chemical Technology & Biotechnology*, se llevó a cabo la aplicación del reactivo Fenton bajo diferentes condiciones. Se modificó el tipo de catalizador, usando Fe(III) y nZVI, y se probó la combinación simultánea de oxidación química (PS + Fe(III)) con lavado de suelo (*soil washing*) usando

dodecil sulfato de sodio (SDS) como surfactante. Se estudió la influencia de la concentración de catalizador y oxidante en la eficiencia de eliminación de fenantreno (PHE), antraceno (ANT), pireno (PYR) y benzo(a)pireno (BaP). Se consiguió prácticamente una total eliminación de ANT y BaP en todos los tratamientos realizados, por lo que las diferencias, en términos de eficacia del tratamiento, entre las distintas técnicas sólo se pudieron comparar por las conversiones de PYR y PHE. En definitiva, la aplicación del reactivo Fenton convencional a la mayor concentración ofreció los mejores resultados en términos de eficiencias de eliminación de los contaminantes.

- **Persulfato activado en discontinuo (Peluffo et al., 2016):** La aplicación de persulfato activado bajo diferentes métodos de activación, para la eliminación de PAHs en un suelo contaminado se encuentra descrita en la publicación titulada *"Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil."* 2016, 563-564. 649-656. Peluffo M, Pardo F, Santos A, Romero A. publicada online en la revista *Science of The Total Environment*. El principal objetivo de este trabajo fue probar diferentes métodos de activación de persulfato y estudiar su efecto en la eficiencia de eliminación de los contaminantes. Además del estudio de las eficiencias de eliminación de los contaminantes se establecieron modelos cinéticos basados en cinéticas de pseudo-primer orden con objeto de profundizar y comprender el comportamiento de la degradación de dichos contaminantes y del oxidante. Los métodos de activación que se consideraron fueron activación con Fe(II), Fe(III) y con nZVI. Aunque la adición de Fe(III) no conlleva una activación directa de persulfato, la presencia de especies reductoras en la matriz pueden reducirlo a Fe(II), en este sentido, la adición de Fe(III) puede actuar como fuente continua y dosificadora de Fe(II). Análogamente, la presencia de nZVI también actúa como fuente dosificadora de Fe, al oxidarse progresivamente el hierro en estado de oxidación cero a Fe(II). Los resultados experimentales mostraron una mejor eficiencia de eliminación bajo la activación con nZVI y la misma tendencia hacia la eliminación de los contaminantes, donde ANT y BaP se eliminaron casi en su totalidad, mientras que PHE y PYR mostraron una mayor resistencia a la degradación.

- **Aplicación de persulfato activado en columna (Pardo et al., 2016b):** En base a los experimentos realizados en batch, el trabajo titulado *"Fate of iron and polycycic aromatic hydrocarbons during the remediation of a contaminated soil using iron-activated persulfate: a column study". 2016, 566-567:480-488.* Pardo F., Santos A., Romero. A. Publicada online en la revista *Science of The Total Environment,* se centra en el tratamiento de un suelo contaminado, también con PAH, con persulfato activado por nZVI y Fe(III). El suelo, además de contaminarse artificialmente con PHE, ANT, PYR y BaP, fue envejecido durante 3 meses desde su contaminación artificial hasta su tratamiento. Atendiendo al mismo razonamiento al empleado en los experimentos en discontinuo, la selección de Fe(III) y nZVI se debió a su efecto como fuentes dosificadoras de Fe(II). El Fe(III) reduciéndose a través de especies presentes en el medio, y las nZVI por corrosión ácida o por la oxidación en presencia de los iones persulfato. Los tratamientos se llevaron a cabo durante 25 días. Tras el tratamiento se analizaron los contaminantes y el hierro remanentes en el suelo. Se obtuvieron unos perfiles de concentración de contaminantes y de hierro lábil a lo largo de la columna, donde las mayores eficiencias de eliminación de los contaminantes y las mayores concentraciones de hierro fueron en las regiones más próximas al punto de inyección de los reactivos. Por otro lado, a partir de los modelos cinéticos obtenidos con -experimentos previos en discontinuo, se simularon las conversiones medias de los contaminantes en la columna, observándose un buen ajuste de los resultados experimentales.

SUMMARY

Over the last decades, the increase in environmental concern worldwide has led to a better understanding of a great number of fields closely related to the preservation of the environment. In this perspective, the study of consequences entailed by contamination of soils with organic pollutants has become particularly relevant. Important improvements have been made through the study of the evolution of contaminants fate, their impacts on human health and on the environment, as well as the development of efficient strategies for soil restoration. Besides, all this progress has been especially driven thanks to the creation and evolution of legal frameworks in the majority of developed countries such as the United States (Environment Protetion Agency), the European Union (the corresponding national environmental agencies of the member countries), Australia and/or Canada.

Although the number of organic pollutants which may be present in soil is extremely large, there are common properties which make a persistent pollutant a serious threat to the environment, such as low or negligible solubility in water, hydrophobicity, high affinity to soil organic matter, low volatility and low biodegradability. Therefore, due to the great variety of organic pollutants and the circumstances in which they can be found into the subsoil (as a result of local or diffuse contamination), there is as well a great number of different alternatives for soil remediation. Among them, the application of techniques based on In Situ Chemical Oxidation (ISCO) have emerged as an efficient and cost-effective alternative to the traditional approaches for soil and groundwater remediation, such as bioventing, air sparging or pump-and-treat.

Taking into account that ISCO techniques are based on the release of strong oxidizing species capable of degrading non-selectively a wide range of organic pollutants, special attention has been paid to the use of Fenton's reagent and activated persulfate for the remediation of soils contaminated by highly persistent organic pollutants (POPs). The main advantages of these techniques lie in the release of radicals with high oxidation potential, such as hydroxyl radical in Fenton's reagent ($OH^{\bullet}$, E=2.8 V) and sulfate radicals ($SO4^{\bullet-}$, E=2.6 V) in activated persulfate, which lead to chain

radical reactions. In this regard, total removal efficiencies of target contaminants as well as good mineralization grades can be achieved with these both techniques. Accordingly, the research for the development of the both ISCO techniques has been encouraged in order to increase their application in real cases.

Therefore, the aim of this PhD thesis is to study the application of different approaches of Fenton's reagent and activated persulfate for the removal of several organic pollutants (gasoline type compounds, diesel type compounds and polycyclic aromatic hydrocarbons (PAHs)). Moreover, the monitoring of the diverse species involved during the treatments (oxidant, contaminant, catalyst, pH) allowed to carry out a deep study of the different phenomena inherent to the process that took place.

This thesis is structured according to the research performed for the remediation of a sandy loamy soil artificially contaminated with different kinds of pollutants, ordered by their decreasing solubility in water (ethylbenzene, B20 biodiesel blend and PAHs). Furthermore, the corresponding experimental results and analysis of each section are detailed in articles published in scientific journals, included in the Journal Citation Reports – Science Edition (JCR), focused on Environmental and Chemical Engineering. On the whole, this thesis contributes to the development and performance of the application of Fenton's Reagent and activated persulfate for the remediation of soils contaminated by POPs. The structure of this PhD thesis is detailed below.

i. <u>Ethylbenzene as representative pollutant of gasoline type compounds.</u>

- **Modified Fenton's Reagent in batch:** This research was focused on the treatment of a soil polluted with ethylbenzene, one of the most persistent pollutants among BTEX. Ethylbenzene is frequently found in soils after gasoline exposure for long periods due to its low volatility compared to the rest of BTEX and ability of interacting with soil organic matter. The publication "*Remediation of soil contaminated by NAPLs using modified Fenton reagent: application to gasoline type compounds.*". Journal of Chemical Technology and Biotechnology 2015; 90: 754-764. Pardo F, Rosas JM, Santos A, Romero A., reports the application of Modified Fenton's Reagent for the remediation of a ethylbenzene-contaminated soil. Sodium citrate tribasic was used as chelating agent and the remediation experiments were carried out under near neutral conditions without pH adjustment. It was studied the influence of the oxidant

dosage, catalyst dosage (Fe(III)) and contaminant load on the removal efficiency of the pollutant. Finally, the evolution of the remaining concentrations of chelating agent, pH, oxidant and contaminant were studied within reaction time. Higher ethylbenzene removal efficiencies were reached with the higher oxidant/contaminant ratios. Nevertheless, higher contaminant loads in soil affected the rate of oxidant consumption, due to the effect of ethylbenzene as radical scavenger and to the mass transfer limitations between the organic phase and the aqueous. The maximum concentration of pollutant in the aqueous phase, where the reaction takes place, is determined by its solubility in water.

ii. Biodiesel blend type compounds (FAME and aliphatic hydrocarbons).

- **Modified Fenton's reagent in batch:** In order to test the effectiveness of Modified Fenton's reagent towards more persistent pollutants than gasoline type compounds, this technique was applied for the remediation of a biodiesel blend contaminated soil, as reported in the published work *"Remediation of a biodiesel blend-contaminated soil by using a modified Fenton process*." Environmental Science and Pollution Research 2014; 21: 12198-12207. Pardo F, Rosas JM, Santos A, Romero A. This work was focused on the evaluation of the removal efficiency of pollutants with very different nature in liquid fuel, selecting a B20 biodiesel blend as a representative example. Taking into account the good removal efficiencies obtained when Modified Fenton's Reagent was used for the removal of ethylbenzene, this technique was also tested towards B20 biodiesel degradation. With this purpose, remediation was carried out under different conditions, modifying the oxidant dose, catalyst concentration, contaminant load and the presence of chelating agent. Higher removal efficiencies of contaminant were obtained without addition of chelating agent, with higher oxidant concentrations and lower contaminant loads. Therefore, it was found that the addition of sodium citrate as chelating agent did not help in the contaminant abatement, as it was a competitor for the oxidation. In addition, it was demonstrated that chelating agent oxidation was higher than contaminant degradation, as the oxidation takes place in the aqueous phase and the solubility of B20 biodiesel was negligible compared to that of the chelating agent. In terms of pollutant abatement, the removal

efficiency towards fatty acid methyl esters (biodiesel fraction) was much higher than the aliphatic compounds (fossil diesel fraction).

- **Activated persulfate in batch:** The best results obtained after the treatment with Modified Fenton's Reagent corresponded to the most aggressive and least feasible options to implement in real cases. Thus, the need to look for an efficient alternative which implies both good removal efficiency and good stability of the oxidant in soil leaded to the study of the remediation of a biodiesel blend contaminated soil by using activated persulfate. This background served as a building block for the development of the published work entitled *"Remediation of a Biodiesel Blend-Contaminated Soil with Activated Persulfate by Different Sources of Iron* Water Air and Soil Pollution 2015; 226: 12. *"*. Pardo F, Rosas JM, Santos A, Romero A. Accordingly, in order to find an efficient way for persulfate activation to remove biodiesel from a contaminated soil, different alternatives were tested. Iron chelated, Fe(II), granular particles of zerovalent iron and nanoparticles of zerovalent iron were used. As in the previous study, regarding iron chelate activation, it was noticed that it was not efficient to remove such a persistent and low water soluble pollutant. On the other hand, the best contaminant conversion was obtained under activation with nZVI. On the whole, more than 60% of biodiesel B20 removal could not be obtained, even under successive addition of nanoparticles of zerovalent iron. However, removal efficiencies of fatty acid methyl esters were practically total, while aliphatic hydrocarbons showed the highest resistance to degradation.

iii. Polycyclic aromatic hydrocarbons

- **Fenton's reagent and modifications in batch:** The study of the remediation of a PAHs contaminated soil by different alternatives to catalyze the Fenton's process is detailed in the published paper entitled "*Optimization of the application of the Fenton chemistry for the remediation of a contaminated soil with polycyclic aromatic hydrocarbons."*. Journal of Chemical Technology & Biotechnology. 2016. 91:6, 1763 – 1772. Pardo F, Peluffo M, Santos A, Romero A. In this work, it was carried out the comparison between Fenton catalysis with Fe(III), nanoparticles of zerovalent iron and the coupling with a surfactant. Concentration of oxidant and catalyst were tested for the

remediation of a soil contaminated with 100 $mg \cdot kg^{-1}$ of each phenanthrene (PHE), anthracene (ANT), pyrene (PYR) and benzo(a)pyrene (BaP). BaP and ANT were removed almost completely in all runs tested while PHE showed the highest resistance. However, the best results regarding contaminants removal efficiency were obtained through the application of Hydrogen peroxide catalyzed with Fe(III) (Fenton like reaction) under the highest catalyst concentration and the use of surfactant improved slightly the pollutant removal efficiencies.

- **Activated persulfate in batch:** The use of activated persulfate, and their different alternatives of activation, for the removal of PAHs from a contaminated soil, is explained in the published research paper *"Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil."* Science of The Total Environment. 2016. 2016. 563–564, 649–656. Peluffo M, Pardo F, Santos A, Romero A. The main purpose of this work was to study the effect of different persulfate activators, through the addition of a Fe(II) sulfate salt, nZVI and Fe(III) sulfate salt. Although is not possible to activate persulfate directly by Fe(III) addition, the presence of reducing species present in soil may reduce it to Fe(II), thus promoting Fe(II) activation acting as a continuous release of iron, as well as the addition of nZVI. Experimental results showed a similar trend in terms of BaP and ANT conversion with respect to the experiments under Fenton's reagent. Therefore, conversions of PHE and PYR were the differentiated factors for the comparison of the effectiveness of the different ways of activation. In this regard, the highest efficiency was obtained when activation was performed by nZVI, similarly to the experiments for the removal of biodiesel by using activated persulfate. Furthermore, the behavior of the contaminants removal matched with pseudo-first order kinetics.

- **Application of activated persulfate in column:** Based on the experiments carried out in batch mode, the published work entitled *"Remediation of a soil contaminated with polycyclic aromatic hydrocarbons by activated persulfate: A Laboratory Scale Column Study".* Pardo F., Santos A., Romero. A. Science of The Total Environment 2016. *Submitted* was based on the application of activated persulfate with nanoparticles of zerovalent iron and Fe(III) for the

remediation of a PAHs contaminated soil. It is noteworthy that the soil, besides of being artificially spiked, it was aged for three months until treatment. The selection of Fe(III) and nZVI as activators was due to the fact that both species can act as continuous releases of Fe(II), Fe(III) from its reduction to Fe(II) by certain species present in the matrix and nZVI oxidation to Fe(II) by the presence of persulfate anions and or acid corrosion. After 25 days treatments there were found profiles of contaminant concentration, as well as iron concentration along the column, being the nearest section to the columns those with higher contaminants conversion and higher iron concentrations. Furthermore, the estimation of the experimental values from the development of the kinetic models carried out in the experiments in batch found a good match between estimated values and average values referred to the whole column.

1.

INTRODUCTION

1.1. Importance of soils

The inestimable value of soils can be explained from an environmental and socio-economic outlook, as it is a dynamic product of the interactions between the most important systems on earth. It provides food, biomass, raw materials and habitat to living, being as well as it acts as a support for human activities, keeps priceless information from the past and also promotes genetic diversity (Muggler et al., 2006; Swartjes et al., 2008). Unfortunately, despite its importance as non-renewable source, due to its extremely slow formation, care of soils and the assessment of human threats to it have been scarcely valued, underestimated or even ignored until recently. The exponential growth of world population is leading to a steady decrease in the land available *per capita*, however, although the majority of human activities are focused on cultivating crops, where the shallower layers of soils are involved, industrial development has seriously compromised the ability of soil to restore itself (resiliency), through atmospheric deposition, leaks, accidents or disposal of waste materials, among others, resulting in a modification of the composition of the original soil (Bridges and Van Baren, 1997).

Soil's ability to carry out its key functions in the ecosystems can be irreversibly affected by soil contamination, by means that once exceeded a certain threshold value of contaminant load, thus surpassing its buffering and self-restoring capacity, soil can be considered functionally dead (EC, 2013). In this sense, consequent problems such as water pollution, high levels of contaminants in plants, human contact with polluted soil and dangers from landfill gases become a serious matter of increasing concern (EEA, 2007).

1.2. Soil contamination

In order to clarify whether a soil can be considered contaminated, for the decision taking of the corresponding measures for its remediation, official institutions have defined the term contaminated soil. For instance, the European Commission proposed the following definition of "contaminated site": *a site where there is a confirmed presence, caused by human activities, of hazardous substances to such a degree that*

they pose a significant risk to human health or the environment, taking into account land use (COM, 2006). Local soil contamination occurs where intensive industrial activities, inadequate waste disposal, mining, military activities or accidents have introduced excessive amounts of contaminants. Soils only have a limited ability to process these contaminants, through filtering or transformation, for example. (EC, 2013).

Regarding the extent of soil contamination, there is a large imbalance in terms of identification of contaminated soils. According to this, developed countries (e.g. United States, European Union, Canada, etc.) have a legal framework to identify and deal with soil contamination, which permits to have an accurate estimation of the number of contaminated or potentially contaminated sites. Nevertheless, in case of developing countries, the lack of government regulation results in a lack of knowledge of the extent of soil contamination.

However, in accordance to government estimations, approximately 384000 soils in the United States, 30000 soils in Canada and 342000 across the European Union are considered as contaminated soils nowadays.

Particularly, in the European Union, that number represents about a 14% near the total of potentially contaminated sites, which may be around 2.5 million. Moreover, about one third of the estimated contaminated soils have been already identified, and about a 15% have been remediated, as shown in Fig. 1.1.

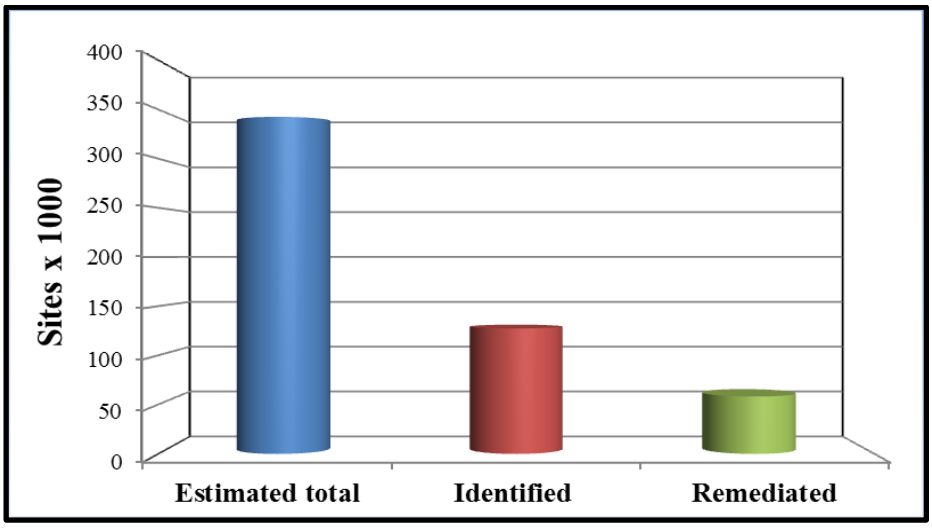

Fig 1.1. Current situation of contaminated soils in Europe. (EIONET, 2011).

1.2.1. Regulations and laws

Legal status regarding contaminated soils has its origin in the United States, with the creation of the Environmental Protection Agency (EPA) in 1970, whose first goal was to identify the impact of the activity in the society of the United States (e.g. industry, transport, waste disposal, etc.) on the quality on air, water and soil. In this background, as a result of the increasing concern regarding soil contamination, in 1980 the US congress created the Superfund program, which is still in force, responsible for cleaning up some of the nation's most contaminated land and responding to environmental emergencies, oil spills and natural disasters.

With regard to Europe, although in 1972, through the declaration of the European charter on soil by the European Council, served as prelude for soil legislation, no important measures were taken until the earlier 80's, where Germany, Netherlands and Belgium were pioneers in the implementation of regulations, based on the previous American model, for the identification and treatment of contaminated lands.

Due to the fact that not all members of the European Union have specific legislation on soil protection, the EU organisms have only impulse some policies in agriculture, water, waste, chemical and prevention of industrial pollution which indirectly help to the protection of soils.

However, valuable data can be found regarding the advances in the last years on soil protection. Since 2001, the European Environment Agency (EEA) in cooperation with EEA affiliated countries started to develop a core set of policy relevant indicators, among which the indicator "Progress in the Management of Contaminated Sites" (CSI015) was the only one related to soil. Since then, data collections in relation to this indicator were launched four times by EEA, the last one in 2006, with contribution from member countries of the European Environment Information and Observation Network (EIONET).

Particularly, in Spain, actions related to soil identification and measure taking started in 1991, with a "National Inventory of Contaminated Soil", by the Spanish Ministry of Public Works, Transport and Environment, which was based on the identification of the potentially contaminant activities. From that inventory, later in

1995, it was developed the National Plan of Soil Recovery for the next decade 1995-2005. The following bullet points summarize the purpose of the plan (Royal Decree, 9/2005):

- Create a legal definition of contaminated soil.
- Make a list of the most likely causes of contamination.
- Decide whether a site is contaminated or not through the establishment of criteria and standards.
- Present technical and financial guidelines to treat and recover properly the contaminated soil.

The Royal Decree 9/2005 was reinforced subsequently in 2011 by the Law 22/2011, of wastes and contaminated soils, emphasizing on the obligation, among other points, for the responsible part of soil contamination, to carry out the corresponding remediation tasks.

1.2.2. Impact on human health

Although for a long time it has been reported the importance of soils for human health, it was not until the 20th century where this recognition started to be considered more from a scientific approach rather than historical evidence. Despite it has been noticed an important progress in the study of the influence of contaminated soils on human health, it is still necessary a deeper multidisciplinary research involving soil science, geology, geography, anthropology, biology, public health, among others. (Brevik and Sauer, 2015). The way contamination affects human health can occur through direct contact (inhalation or skin contact) or indirectly by ingestion through the food chain.

However, a contaminant becomes toxic or carcinogenic in the human body when it is noticed an overload of the detoxification systems of the organs, mainly liver and kidneys. At this point, the body starts to be exposed to excess amounts either of the chemical itself or of a metabolite produced when the body's normal metabolic pathways (the means of processing the toxic compound) are saturated. (EA(UK), 2009).

Some practices and facts that can normally compromise human health are summarized as follows, as reported by the European Commision (EC, 2013) and Van Camp et al. (Van-Camp et al., 2004):

• The most frequent cases of point sources occur when handling spills or accidents, probably the concentration of pollutants is not significant, but its continual release to the media increases the risk.

• Municipal waste disposal, energy production and transport, mainly in urban areas.

• Past activities and poor management practices, as a result of the legacy of inefficient technologies and uncontrolled emissions. Former military sites, abandoned industrial facilities and storage sites which may still be releasing pollutants to the environment are crucial factors affecting greatly groundwater contamination and related health problems.

• The soil's capacity and resilience in terms of holding onto and transforming contaminants mean that damage is not noticed until it is far advanced.

To understand the extent of this situation, it can be seen in Fig. 1.2, which summarizes the main activities that result in soil contamination, as average percentages in the European Union (EIONET, 2011), that near 70% of the key sources of soil contamination come from waste disposal, water treatment, industrial and commercial activities.

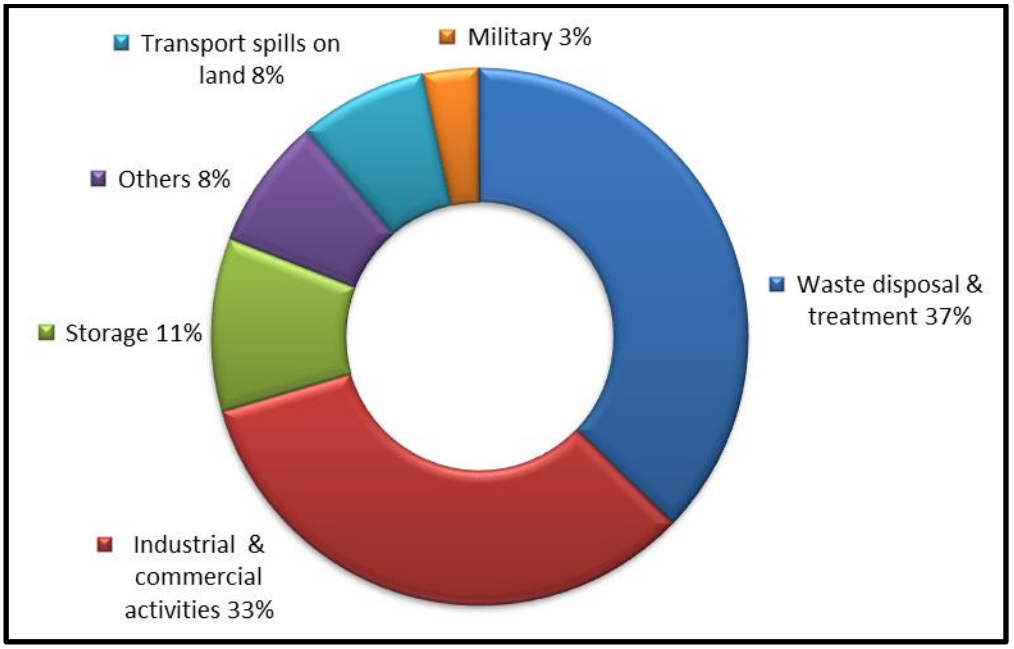

Fig. 1.2. Key sources of soil contamination (EIONET, 2011).

1.2.3. Types of contaminants and fate

1.2.3.1. Types of contaminants

The number and variety of possible contaminants that can be present in soils is as high as is the number of chemical compounds. Besides that, taking into account the development of organic chemistry in last years, the number of different contaminants in soils is reaching many thousands of compounds.

Soil contaminants can be classified in two main groups, heavy metals or organic pollutants. According to the average distribution in the European Union (EIONET, 2011) of type of chemicals found in contaminated soils, as shown in Fig. 1.3, heavy metals are the main pollutants in 34.8 % of contaminated sites in Europe, while the remaining belongs to different types of organic pollutants (mineral oils, polycyclic aromatic hydrocarbons, aromatic hydrocarbons, etc.).

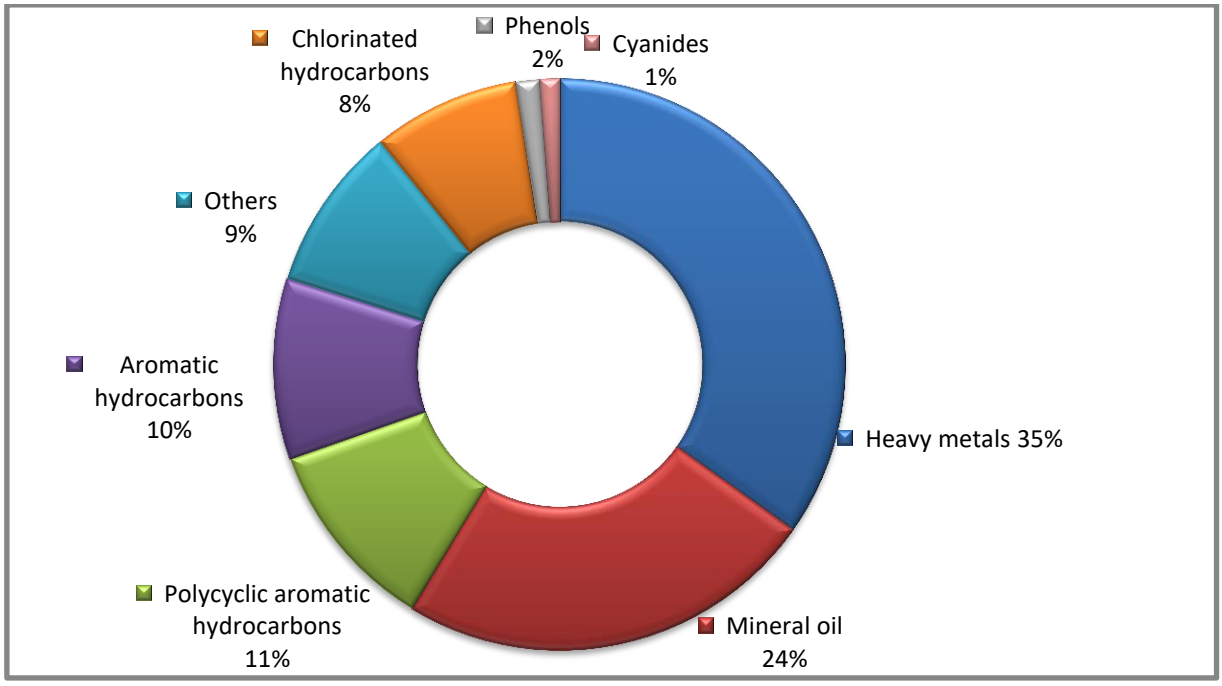

Fig. 1.3. Contaminants affecting the soild matrix in Europe. (EIONET, 2011).

Taking into account that some semi-metals or metalloids elements, such as arsenic or antimony, are often included in the heavy metals group, it is usually found that this group is called as trace elements group (EC, 2013). In this sense, this group generally includes the contaminants listed below:

• Arsenic (As)

• Lead (Pb)

• Cadmium (Cd)

• Hexavalent Chromium (Cr VI) (the other Cr forms are not toxic)

• Copper (Cu)

• Mercury (Hg)

• Nickel (Ni)

• Zinc (Zn)

Among all carbon-based pollutants (organic pollutants), persistent organic pollutants (POPs) are those which represent a highest environmental impact as well as a biggest threat for human health. As this kind of pollutants possess a very low solubility in water, they are usually found in groundwater or soils in the form of Non Aqueous Phase Liquids (NAPLs). Besides, if the density of this kind of pollutant is higher than water, they are defined as Dense Non Aqueous Phase Liquids (DNAPLs) or Light Non Aqueous Phase Liquids (LNAPLs) (Lapinskiene et al., 2006; Molina-Barahona et al., 2005). This fact is due to their high resistance to biodegradation, as they consist in organic molecules that do not break down easily in the environment. Therefore, the most important types of POPs found in contaminated soils are:

• Polychlorinated biphenyls (PCBs)

• Polybrominated biphenyls

• Polychlorinated dibenzofurans (PCDFs)

• Polycyclic aromatic hydrocarbons (PAHs)

• Organophosphorus and carbamate insecticides (pesticides)

• Herbicides

• Organic fuels (gasoline, diesel)

• Pharmaceuticals and their metabolites

1.2.3.2. Fate of contaminants

Depending on the physicochemical properties of soils, the behavior of contaminants can be highly variable. If contaminant belongs to the group of heavy

metals or metalloids, properties such as reduction/oxidation potential, absorption/desorption capacity and pH are the most important. On the other hand, the amount of soil organic matter (SOM) mainly affects the way an organic pollutant can be retained or released from the soil. For instance, a strongly-bonded contaminant is less likely to be released from the soil into the groundwater or as vapor phase. (Brevik and Burgess, 2012). Since them normally have a high retention capacity for hydrophobic compounds, soils work as effective sinks of POPs. However, depending on several factors, such as climatic conditions, possibility of wet and dry atmospheric deposition, leaks from piping or storage, distance to the phreatic level, etc., soils can act as long-term storage systems for these contaminants or even as sources of pollution to the air (especially in summer, due to volatilization) or water. (Holoubek et al., 2009). Particularly, in case of POPs, decades are enough to reach a steady state of emissions between releases and losses given their high residence time and overall half-life in the environment, which are inversely proportional to the transformation rate constants for air, water and soil (Jones and de Voogt, 1999).

1.2.4. Contamination by petroleum hydrocarbons

Hydrocarbon exploitation represents one of the most relevant sources of soil and groundwater contamination, thus, leaks or accidental spills from pipelines, road transportation, corrosion or fissures in storage tanks can lead to the penetration deep into the soil of petroleum derived hydrocarbons (fuel oils, diesel oils, gasolines) (de la Vega et al., 2003). Given the hydrophobic nature, lower density than water and low solubility of these compounds, they tend to either reach the water table in the form of light non-aqueous phase liquids (LNAPLs) or be adsorbed by the soil organic matter, resulting in a dual problem of soil and groundwater contamination. Besides that, due to the semivolatile or volatile nature of some compounds, the release of hydrocarbon vapors to the atmosphere extends the problem to the air. In this sense, as it is represented in Fig. 1.4, contamination by hydrocarbons may exist in a four-phase system, by means soil, water, soil gas and LNAPL (C. J. Newell et al., 1995).

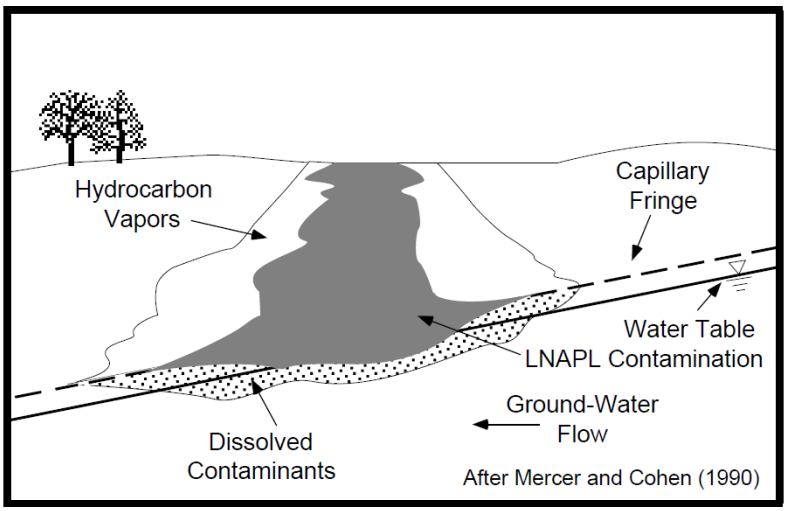

Fig. 1.4. Simplified conceptual model for LNAPL release and migration (C. J. Newell et al., 1995).

1.2.4.1. Gasoline type compounds (ethylbenzene)

Gasoline is an organic mixture of more than 150 different types of chemicals which comes as the second lighter fraction in the fractional distillation of petroleum. Since it is used as fuel for internal combustion engines in several types of automobiles and other vehicles, its properties are normally improved, in order to meet the standards, by the addition of additives. Gasoline may be presented as a colorless, pale brown or pink liquid, it is highly flammable (flash point -43 ºC) and volatile (ATSDR, 1995b).

Since gasoline is a mixture of organic compounds with a wide variation in their physical and chemical properties, such as cycloalkanes, alkenes or aromatics, the fact of finding gasoline itself in the environment is quite unlikely. In this regard, the most volatile compounds will tend to partition to the atmosphere, those which higher solubility will be more likely to appear dissolved in water and the most lipophilic compounds with higher boiling points, will tend to be bonded to the soil organic matter (ATSDR, 1995b).

Therefore, critical environmental and health effects from hydrocarbon contaminated soils have led to an increase in the efforts for the development and implementation of innovative technologies to carry out an efficient cleanup of affected sites (Rahman et al., 2002), as it is more deeply detailed in “remediation techniques” section.

Volatile compounds in gasoline are normally degraded by sunlight in the air, taking hours or even weeks until their abatement. On the other hand, the most soluble chemicals are usually broken down in water by natural processes; in this regard, it is quite unlikely to find high levels of these contaminants in plants or animals. With respect to gasoline compounds present in soil, potential sorption is highest for alkenes, followed by aromatics, cycloalkanes and least for alkanes. However, depending on several factors, such as soil properties (pH, hydrogeological conditions, soil organic matter content, metal content, etc.), size of the spill, gasoline hydrocarbons may be retained in the soil pore spaces, if the amount of contaminant is small relative to the distance to the groundwater. Otherwise, if the amount is large relative, gasoline hydrocarbons can reach the water table, spreading themselves horizontally above the phreatic level (Adam and Duncan, 1999; ATSDR, 1995b). Therefore, once gasoline hydrocarbons reach subsoil, biodegradation by fungi or bacteria becomes the main natural process (ATSDR, 1995b; Thomas et al., 1990). Nevertheless, this ability usually is limited, being unlikely to reach the total removal of the contaminants by only natural biodegradation phenomena (Sra et al., 2013).

Among all gasoline components, the fraction represented by Benzene, Toluene, Ethylbenzene and Xylene, known as BTEX, normally represents near 20% of the total hydrocarbons in gasoline (Nadim et al., 2000). Beside this, as toxicity and acute effects of BTEX on human health have been widely investigated and demonstrated, representing the majority of the total toxicity in contaminated soils and groundwater by gasoline, (Carroquino et al., 1992; Kang and Hua, 2005), these pollutants are considered as priority pollutants and their presence in drinking water must be strictly controlled. For instance, the US EPA have stablished maximum concentration levels of 0.005 $mg \cdot L^{-1}$ for benzene, 1.0 $mg \cdot L^{-1}$ for toluene, 0.7 $mg \cdot L^{-1}$ for ethylbenzene, and 10.0 $mg \cdot L^{-1}$ for xylenes, respectively (Pardo et al., 2014).

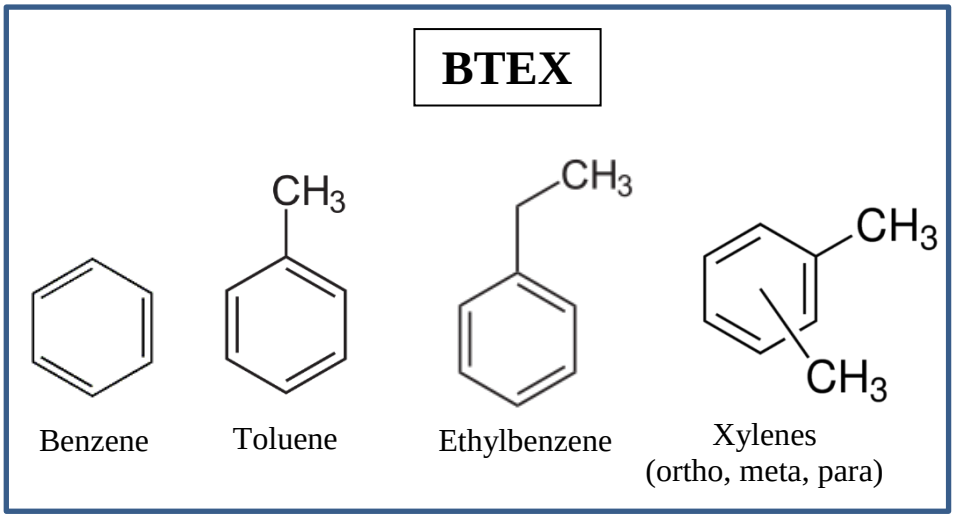

Fig. 1.5. BTEX simplified molecular structures.

Particularly, the interest arisen in this work focused on the removal Ethylbenzene of a contaminated soil lies on its particular behavior among all BTEX, as it possess the lowest vapor pressure and the highest resistance to degradation techniques, as well as it is one of the major species found in contaminated soils by gasoline (Kang and Hua, 2005; Lapinskiene et al., 2006).

1.2.4.2. Biodiesel blend compounds (aliphatic hydrocarbons & fatty acid methyl esters)

According to the ASTM D6751, biodiesel blends are defined as a blend of biodiesel fuel with petroleum-based diesel fuel, designated BXX, where XX represents the volume percentage of biodiesel fuel in the blend. Basically, the chemical composition of biodiesel blends consists of aliphatic hydrocarbons, normally ranging from number of carbons between C12 to C20, which come from the petroleum-based diesel fuel, and fatty acid methyl esters, known as FAME, which are the main compounds in biodiesel formulations. The importance of biodiesel consumption, as an alternative, or even as a complement to traditional petroleum based diesel, along the last decade has been of important growth, as it has similar physico-chemical properties of to those of fossil diesel fuel, and can therefore totally or partially replace fossil diesel fuel in compression ignition engines (Pasqualino et al., 2006). In this sense, its use in regular vehicle engines has been encouraged by the governments, in the form of the great number of biofuel directives during the last decade worldwide, where minimum

mandatory percentages of biodiesel in blending are being established (Sadhukhan and Ng, 2011).

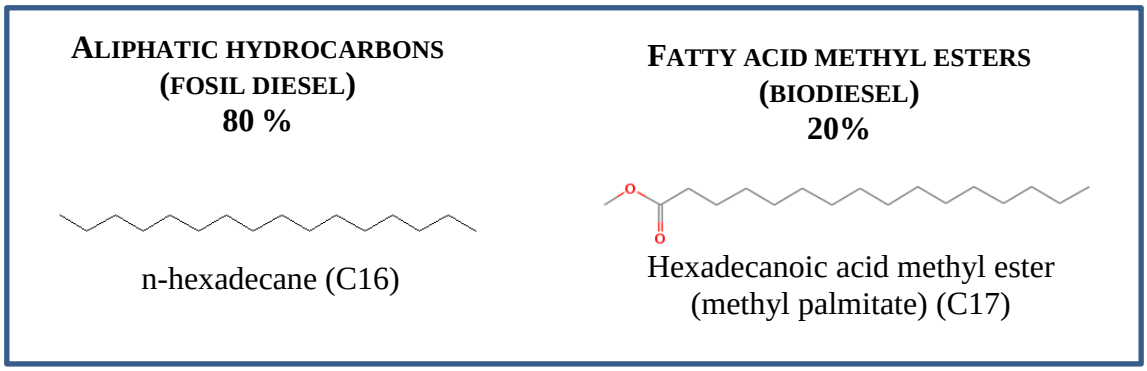

Fig. 1.6. Representative chemicals present in fosil diesel and FAME. Simplified molecular structures.

Diesel fuel, as well as gasoline, is obtained from the fractional distillation of petroleum. Nevertheless, Diesel fuel is mainly a mixture of aliphatic hydrocarbons ranging from 12 and 20 number of carbons, (C12 to C20), as it is obtained from a heavier fraction than gasoline during the fractional distillation, being a kind of fuel oil. Indeed, fuel oils are classified in 6 different categories according to their boiling point and average carbon chain length; since fuel oil no.1, where jet fuel or kerosene are included, to fuel oil no.6, a highly viscose residual oil, used basically for marine purposes. In this sense, Diesel fuel for automobiles is commonly known as fuel oil no. 2-D (ATSDR, 1995a). On the other hand, given the low solubility of diesel compounds in water, which is much lower than that corresponding to gasoline type compounds, the hydrophobicity and the resistance to biodegradation, Diesel fuel tends to adsorb to soil particles and to interact to soil organic matter. Besides this, if the dimension of the spill is large enough, Diesel can reach, as well as it was the case of gasoline, the water table, thus resulting in a dual problem of soil and groundwater contamination (Adam and Duncan, 2002; Adam and Duncan, 1999; Pardo et al., 2014).

On the other hand, regarding biodiesel impact on the environment, it is frequently reported as a non-toxic or highly biodegradable pollutant with respect to fossil diesel (Pasqualino et al., 2006). Nevertheless, since its presence as pollutant in soils or groundwater is not as widespread as traditional fossil diesel, due to it have appeared and started to be used in the recent years, knowledge in this subject is still a challenge for environmental research, in terms of increasing efforts trying to elucidate environmental

and health effects as well as the fate of biodiesel (Leme et al., 2012). According to this fact, it can be found in literature some evidences of harmful effects of biodiesel on human health and environment (Leme et al., 2012; Leme et al., 2011; Restrepo-Florez et al., 2013).

Therefore, the criteria of choosing biodiesel as a target contaminant in this work lays on its nature as a mixture of aliphatic hydrocarbons, characterized by its refractory nature to degradation, and biodiesel compounds, represented by the FAME, where there is still lack of research regarding their removal from contaminated groundwater or soils.

1.2.4.3. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) represent a group of more than 100 organic compounds that consist of molecules of two or more fused benzene rings arranged in linear, angular or cluster mode. PAHs appear from incomplete combustion processes from several anthropogenic or natural phenomena, such as activities related to manufactured gas, wood impregnation, hydrocarbon production, coke production, and metal processing facilities metallurgy, volcano eruptions, forest fires among others (Brown et al., 2003; Sims and Overcash, 1983).

Moreover, according to the toxicity and carcinogenic potential of some of them, (e.g. Benzo(a)pyrene, chrysene), PAHs have drawn special attention by a great number of environmental agencies and scientific communities (Tian et al., 2013), as in case of the Environmental Protection agency (EPA) of the United States and the European Environment Agency, where PAHs have been included as priority pollutants. According to their physicochemical properties, as they possess very low solubility in water, low volatility and low and high solid-water partition coefficient, PAHs tend to interact easily to soil organic matter and to accumulate in soils (Hamdi et al., 2006). Thus, regardless the fact that PAHs can be released from various sources, such as public sewage treatment plants, automotive exhaust, irrigation with coke oven effluent, leachate from bituminous coal storage sites and from use of soil compost and fertilizers, these contaminants tend to settle in soils at the end of the contaminant cycle (ATSDR, 1995c).

Nevertheless, the most important contribution to the contamination of soils by PAHs came from the development of manufactured gas plants (MPG) throughout the 19th century. In this regard, their closure and lack of concern about the environmental impact from this activity during the 20th century resulted in the abandonment of an enormous number of contaminated lands, with PAHs as the major pollutant remaining in them (Dor et al., 2000), mainly present in the tar resulting from the coal pyrolysis.

Therefore, PAHs were chosen in this work as their removal from contaminated soils or groundwater represents a real challenge. In this sense, among the great number of different PAHs, anthracene (3 ringed) phenanthrene (3 ringed) pyrene (4 ringed) and benzo(a)pyrene (5 ringed) were selected for the remediation experiments (Fig 1.7).

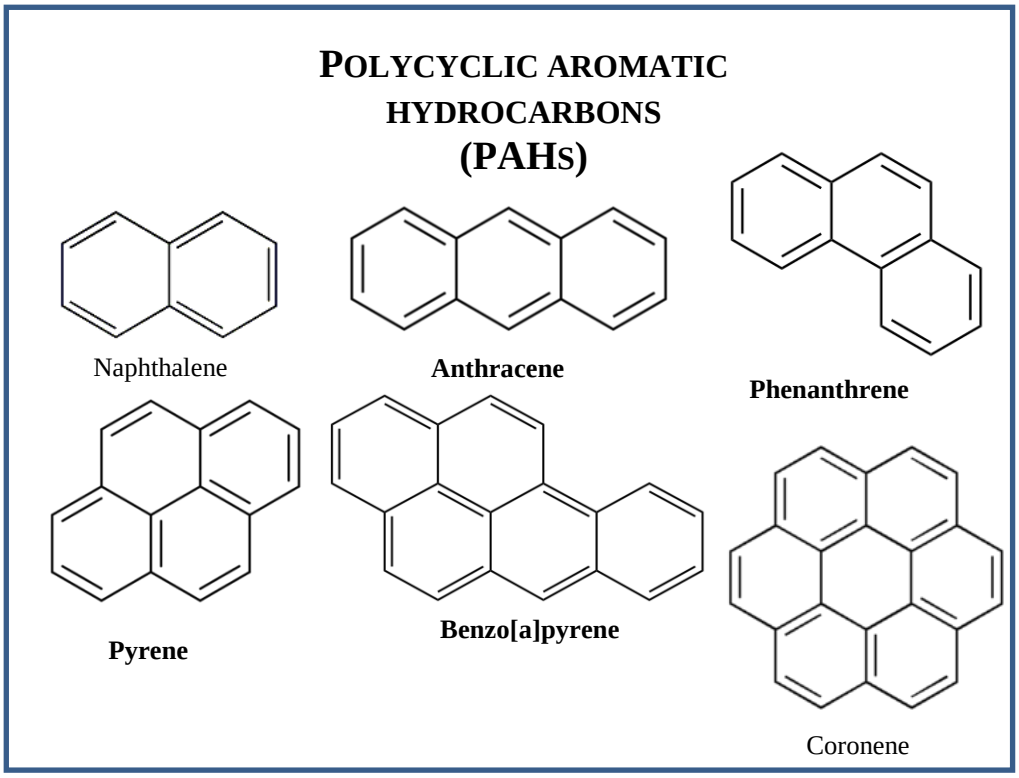

Fig. 1.7. Simplified molecular structures of representative PAHs. PAHs appearing in this thesis are marked in bold.

1.3. Remediation of contaminated soils

The increasing public concern regarding treatment of contaminated sites since the mid-1970s resulted in the emergence of a vast number of new and rigorous environmental regulations around the industrialized countries. This background provided a perfect framework for the development and growth of research in a wide range of disciplines concerned with soil remediation, such as geology, hydrology,

chemistry, microbiology, meteorology, toxicology and epidemiology, as well as chemical, mechanical, electrical, industrial, civil, and environmental engineering (Kuo, 2014). The purpose of soil remediation is to reduce contaminants to acceptable levels in order to restore the soil functions to be suitable for use, which means that environmental risks after remediation can be considered negligible.

On the whole, soil remediation is a part of a sequence of measures for the redevelopment of contaminated sites, which involve previous site characterization, risk assessment of hazards, selection of the most suitable remedial action and completion of site cleanup. Indeed, for the selection of the most appropriate remediation technique, several factors should be taken into account, such as flexibility, compatibility, speed, and cost of each method. A remedial method must be flexible in its application to ensure that it is adaptable to site specific soil and ground-water characteristics. In addition, a remedial method must be compatible with characteristic urban site conditions, including surrounding buildings and utility infrastructure. Most importantly, the economics of site remediation must offer a viable option to development (Reddy et al., 1999).

Accordingly, the reduction of the environmental impact to acceptable levels through the application of the most proper treatment may be carried out to (Nathanail and Bardos, 2005):

- Complete or substantial destruction/degradation of the pollutants.
- Extraction of pollutants for further treatment or disposal.
- Stabilization of pollutants towards less mobile or toxic species.
- Separation of non-contaminated materials, and their recycling, from polluted materials that require further treatment.
- Containment of the polluted material to restrict exposure of the wider environment.

The remediation techniques can be defined as In-situ, where no excavation of the contaminated soil occurs, they generally take a longer time to effect treatment to the desired limits and there is less certainty about the uniformity of treatment because of the inherent variability in soil and aquifer characteristics and difficulty in monitoring progress. On the other hand, there are Ex-situ treatments, consisting in the excavation of a contaminated area (ex-situ approach) and treating the material on the same site (ex-

situ, on-site) or transporting it to a remote site for cleaning (ex-situ, off-site), which can often be more complicated and expensive (Lodolo, 2003).

More specifically, remediation techniques can be also classified in accordance with their mechanisms. In general, remediation technologies can be grouped into categories based on their treatment mechanism: biological, physical, chemical, electrical, and thermal. It is noteworthy to point out that the most traditional approach, excavation and disposal is not included in this list. Likewise, physical, chemical and electrical treatments can be included into one group, called physico-chemical treatments, as they normally occur together in the treatment process. It is also normal to find thermal treatments in a separate group, as well as biological treatments. On the other hand, due to the complex nature of many polluted soils, in many situations, as a consequence of the presence of different types of contaminants, it is frequently necessary to apply several remediation techniques (treatment train) to reduce the concentrations of pollutants to acceptable levels.

Therefore, the main aspects of each group of treatments are listed below:

Biological treatments

Biological treatment is a process whereby contaminants in soil, sediments, sludge or groundwater are transformed or degraded into innocuous substances such as carbon dioxide, water, fatty acids and biomass, through the action of microbial metabolism.

Biological processes are typically implemented at low cost. Contaminants can be destroyed and often little to no residual treatment is required. However, the process requires more time and it is difficult, in general, to determine if contaminants have been completely destroyed. Another drawback to biological treatments lays in the fact that microbes may often be sensitive to toxins or highly concentrated contaminants in the soil.

Physicochemical Treatments

Physicochemical treatments use the physical, chemical and/or electrical properties of the contaminants or even the contaminated medium to abate (i.e., chemically convert), separate, or contain the contamination. In the physical processes the phase

transfer of pollutants is induced. In the chemical processes the chemical structure, which determines the behaviour of the pollutants, is changed through chemical reactions to produce less toxic or better separable compounds from the solid matrix.

These treatments are typically cost effective and can be completed in short time periods (in comparison with biological treatments). Equipment is readily available and is generally not engineering or energy-intensive. Certain in-situ physico-chemical treatment technologies are sensitive to certain soil parameters. For example, the presence of clay or humic materials in soil causes variations in horizontal and vertical hydraulic parameters, which, in turn, cause variations in physico-chemical process performance.

Thermal Treatments

Thermal treatments, where the driving force of the process is heat, generally offer quick cleanup times but are typically the most costly treatment group. This difference, however, is less in ex-situ applications than in in-situ applications. Cost is driven by energy and equipment costs and is both capital and Operation & Maintenance intensive.

Thermal processes use heat to increase the volatility, to burn, decompose, destroy or melt the contaminants. Cleaning soil with thermal methods may take only a few months or several years. The time it takes depends on three major factors that vary from site to site: type and amounts of chemicals present; size and depth of the polluted area; type of soil and conditions present.

Therefore, given the great number of different type of treatments which can be performed as well as the wide variety of critical factors determining whether one technique can be more suitable than others, there is no a general trend worldwide in which an specific technique is more implemented than other. Indeed, this fact is in agreement with Fig. 1.8, which shows a distribution of the implementation percentage regarding the different types of techniques applied in the European Union for soil remediation.

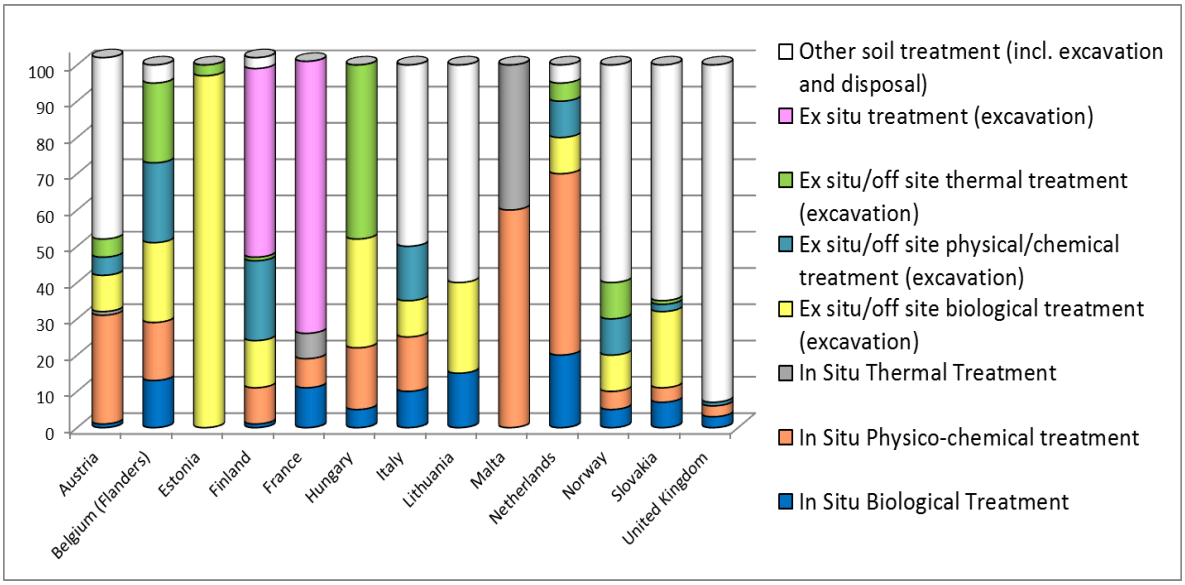

Fig. 1.8. Dominant remediation technologies for contaminated soil sediment and sludge. (EIONET, 2011).

1.3.1. Remediation Techniques: In Situ Chemical Oxidation (ISCO)

Remediation techniques based on In Situ Chemical Oxidation (ISCO) have emerged as a consequence of the evolution of the strategy for soil restoration. According to this, the traditional treatments, such as air sparging, pump-and-treat, bioventing or soil vapor extraction (SVE), apart from the fact that their application normally implies high investments, they have been proven to be efficient in the first stages of treatments, but being progressively less effective as the cleanup goals are being reached, due to mass transport limitations. Besides that, the effectiveness of traditional approaches for the removal of Non Aqueous Liquid Phases (NAPLs) is questioned given that concentration of contaminants may rebound to higher values than the target levels (Baciocchi, 2013) after the treatment as a consequence of not achieving complete removal of the contaminants.

Therefore, the development of ISCO, among a wide range of other alternative technologies to the traditional approaches has grown remarkably within the last 10 to 15 years, as some of them have started to become commercially available through preliminary research and field demonstrations (Baciocchi, 2013).

The advantages of ISCO among other In Situ treatments lie on their moderate costs for high concentration areas, their quick treatment, the possibility of obtaining a complete removal of the contaminants and its compatibility with other In Situ

techniques, like bioremediation. Nevertheless, some drawbacks must be considered for the application of ISCO, as they may not be cost effective for the treatment of dilute plumes, some oxidants have short lifetimes (e.g. hydrogen peroxide), its application may imply health and safety threats, they lose effectiveness against low permeability zones, it is quite likely to observe rebound of the contaminants, and finally, the oxidants may be consumed by materials present in soils, leading to an unproductive consumption (Siegrist et al., 2011).

ISCO treatments consist in the injection of certain reagents, which once reached the subsoil, release highly oxidizing species, creating as a result a reactive zone capable of degrading a wide range of persistent organic pollutants (POPs). In this regard, there is a great number of different techniques which can be applied to meet the cleanup goals. Nevertheless, the most common protocols are catalyzed hydrogen peroxide (also known as CHP or Fenton's reagent), potassium and sodium permanganate, sodium persulfate, and ozone (Siegrist et al., 2011).

The aforementioned techniques are summarized in Table 1.1 as well as the oxidation potential of each of the oxidizing species yielded and their corresponding chemical reactions, during the application of ISCO in Tables 1.1 and 1.2, respectively.

Table 1.1. Main characteristics of the different treatments based on ISCO (Huling and Pivetz, 2006; Siegrist et al., 2011)

Oxidant	*Chemical reagent*	*Comercial form*	*Activator*	*Reactive species*
Permanganate	$KMnO_4$ / $NaMnO_4$	Powder / Liquid dilution	None	MnO_4^-
Hydrogen peroxide	H_2O_2	Liquid	None, Fe(II), Fe(III)	$OH^{\cdot}$, $O_2^{\cdot-}$, $HO_2^{\cdot-}$, HO_2^-
Ozone	O_3 (in air)	Gas	None	O_3, $OH^{\cdot}$
Persulfate	$Na_2S_2O_8$	Powder	None, Fe(II), Fe(III), Heat, H_2O_2, alkaline pH	$S_2O_8^{2-}$, $SO_4^{\cdot-}$

Table 1.1. Main characteristics of the different treatments based on ISCO (Huling and Pivetz, 2006; Siegrist et al., 2011) (continuation).

Oxidant	*Chemical reagent*	*Comercial form*	*Activator*	*Reactive species*
Peroxone	$H_2O_2 + O_3$ (in air)	Liquid / gas	O_3	O_3, $OH^{\cdot}$
Percarbonate	$Na_2C_2O_3 \cdot 1.5H_2O$	Powder	Fe (II)	$OH^{\cdot}$
Calcium peroxide	CaO_2	Powder	None	H_2O_2, HO_2^-

Table 1.2 Main reactive species released to the media during treatment by ISCO.

Reactive species	*Formula*	*Standard reduction potential (V)*	*Most important reaction*
Hydroxil radical	$OH^{\cdot}$	+2.8	$H_2O_2 + Fe^{2+} \rightarrow OH^{\cdot} + OH^- + Fe^{3+}$ $OH^{\cdot} + H^+ + e^- \rightarrow H_2O$
Sulfate radical	$SO_4^{\cdot -}$	+2.6	$S_2O_8^{2-} + (Fe^{2+}$ or heat$) \rightarrow SO_4^{\cdot -} + (SO_4^{2-} + SO_4^{\cdot -})$ $SO_4^{\cdot -} + e^- \rightarrow SO_4^{2-}$
Ozone	O_3	+2.1	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + 2H_2O$ $O_3 + OH^- \rightarrow O_2 + HO_2^{\cdot}$
Persulfate anion	$S_2O_8^{2-}$	+2.1	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$
Hydrogen peroxide	H_2O_2	+1.77	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$
Permanganate anion	MnO_4^-	+1.7	$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2$ (s) $+ 2H_2O$
Perhydroxyl radical	$HO_2^{\cdot -}$	+1.7	$H_2O_2 \rightarrow HO_2^{\cdot -} + H^+ + e^-$
Oxygen	O_2	+1.23	$O_2 + 4H^+ + 4e^- \rightarrow H_2O$
Hydroperoxide anion	HO_2^-	+0.88	$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$
Superoxide anion	$O_2^{\cdot -}$	-2.4	$O_2 + e^- \rightarrow O_2^{\cdot -}$

Although permanganate has been the most widely implemented technique in real cases among ISCO techniques (Krembs et al., 2010), the potential shown of Fenton's reagent and activated persulfate over the last years, has resulted in an increasing number of scientific contributions in the form of articles and the growth in the implementation of real case applications (e.g. ISOTEC). On the whole, these developments have made these techniques a feasible and practical approach for the remediation of a great number of contaminated soils by POPs. In this sense, given that each technique has its specific advantages and disadvantages; its implementation depends on several factors, such as treatment costs, effectiveness against the target pollutant, stability of the oxidant in soil, possibility of releasing byproducts, among others. The most characteristic properties of each remediation technique are shown in Table 1.3. Therefore, it would not be appropriate to talk about a better/worst remediation technique in absolute terms, but in terms of suitability under certain conditions.

Table 1.3. General aspects of the most popular ISCO technologies.

Property	*Sodium/ potassium permanganate*	*Activated sodium persulfate*	*Modified Fenton's reagent*	*Traditional Fenton's Reagent*	*Ozone*
Persistence in subsurface (Halflife)	High (days)	Medium to High (hours to days)	Medium (hours)	Low (Minutes)	Low
Precipitation	Black MnO_2. Decreases soil permeability	Iron (slightly) Not remarkable changes on permeability	Iron (slightly) Not remarkable changes on permeability	Dark brown iron hydroxide Iron fouling and decrease soil permeability	-
Ability to desorb contaminants	Limited	Limited	Effective	Limited	Limited
pH/alkalinity	Effective at natural subsurface pH (5-8)	PS solution lowers native soil pH. PS can be activated under alkaline conditions	Wide range (2-10)	Requires pH< 3.5	Wide range
Treatment costs (strongly depend on soil NOD)	Low $KMnO_4$ similar to Fenton's $NaMnO_4$ more expensive than $KMnO_4$	Low More expensive than Fenton's and $KMnO_4$ Cheaper than $NaMnO_4$	Low Similar or cheaper than PS and $KMnO_4$	Low Similar than Modified Fenton's	High

Table 1.3. General aspects of the most popular ISCO technologies (continuation).

Property	*Sodium/ potassium permanganate*	*Activated sodium persulfate*	*Modified Fenton's reagent*	*Traditional Fenton's Reagent*	*Ozone*
Possibility of reaction outgases	Not noticeable	Not noticeable	Gas formation in form of CO_2, H_2O and O_2	More aggressive gas formation in than Modified Fenton's	Gas formation
Matrix treatment	Effective in groundwater treatment. Less effective against soil bound contaminant treatment	Effective in groundwater treatment. Less effective against soil bound contaminant treatment.	Effective in groundwater treatment. May be effective against soil bound contaminant treatment	Effective in groundwater treatment. May be effective against soil bound contaminant treatment	Effective in groundwater treatment. May be effective against soil bound contaminant treatment

1.3.2. Conventional Fenton's Reagent

As it was aforementioned, Fenton's reagent is based on the release of strong hydroxyl radicals through the combination of hydrogen peroxide and a transition metal, preferable Fe. Although reaction chemistry of hydrogen peroxide is complex, due to a great number of radical reactions take place, Fenton's reagent is capable of degrading non-selectively a wide range of organic pollutants (Baciocchi, 2013).

For the release of hydroxyl radicals, hydrogen peroxide can be catalyzed by Fe(II) and Fe(III), iron and manganese soil minerals and other metals in solution. These catalysts may be present in the soils matrix, or added during treatment in order to improve the efficiency of the treatment. Fenton's reagent was firstly applied for wastewater treatment, but thanks to the development of environmental industry, it has been adapted for soil and groundwater remediation (Siegrist et al., 2011).

Given the complexity of the chemistry involved in the use of Fenton's reagent, it has been used the term "catalyzed hydrogen peroxide propagations". In this sense, not only the formation of the hydroxyl radical, but a pool of different radicals appearing during the process, such as perhydroxyl radical ($OH_2^{\cdot -}$), superoxide anion ($O_2^{\cdot -}$) or hydroperoxide anion (HO_2^-), play an important role during the chain reactions (Kiwi et al., 2000).

There has been a deep research during years in order to clarify the mechanisms of Fenton's process, either if under activation via iron in solution or mineral iron, etc. In this sense, a great number of reactions have been identified, as reported in the literature (De Laat and Gallard, 1999; Haber and Weiss, 1934; Watts and Dilly, 1996). Accordingly, reactions can be classified as initiation reactions, from oxo-hydroxo iron complexes Eqs. [1.1] or [1.2] or Fe(II) Eq. [1.3], by means of the formation of the radical species; chain propagation reactions (Eqs. [1.4] to [1.8], where the radicals react in chain taking place the formation of new radicals; and chain termination reactions, when no radical is formed as product reaction Eqs. [1.9] to [1.12] (Kiwi et al., 2000; Watts and Dilly, 1996).

Initiation

$FeOOH^{2+} + FeOH^{2+} \rightarrow 2 \cdot Fe^{2+} + O_2 + H_2O$	$k = 2 \cdot 10^{-3}\ (s^{-1})$	[1.1]
$FeOOH^{2+} \rightarrow Fe^{2+} + HOO^{\cdot}$	$k = 5\ (M^{-1} \cdot s^{-1})$	[1.2]
$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^{-}$	$k = 53\ (M^{-1} \cdot s^{-1})$	[1.3]

Chain propagation

$OH^{\cdot} + H_2O_2 \rightarrow HOO^{\cdot} + H_2O$	$k = 3.0 \cdot 10^{7}\ (M^{-1} \cdot s^{-1})$	[1.4]
$HOO^{\cdot} + Fe^{3+} \xrightarrow{-H^{+}} Fe^{2+} + O_2$	$k = 1.0 \cdot 10^{6}\ (M^{-1} \cdot s^{-1})$	[1.5]
$RH + OH^{\cdot} \rightarrow R^{\cdot} + H_2O$	*k = depends on the organic substrate (R)	[1.6]

Chain termination

$Fe^{2+} + HOO^{\cdot} \rightarrow Fe^{3+} + HO_2^{-}$	$k = 8 \cdot 10^{5}\ (M^{-1} \cdot s^{-1})$	[1.7]
$Fe^{2+} + OH^{\cdot} \rightarrow Fe^{3+} + OH^{-}$	$k = 4 \cdot 10^{8}\ (M^{-1} \cdot s^{-1})$	[1.8]
$HOO^{\cdot} + HOO^{\cdot} \rightarrow H_2O_2 + O_2$	$k = 1.8 \cdot 10^{6}\ (M^{-1} \cdot s^{-1})$	[1.9]
$RH + OH^{\cdot} \rightarrow ROH + H^{+}$	*k = depends on the organic substrate (R)	[1.10]
$RH + OH^{\cdot} \rightarrow CO_2 + H_2O$	*k = depends on the organic substrate (R)	[1.11]

Among all these reactions, there are some desirable reactions, such as those in which the organic pollutant is mineralized or degraded (Eqs. [1.6], [1.7], [1.11]), or Fe(III) is reduced to Fe(II) for the regeneration of the catalytic cycle. On the other hand, the non-desirable reactions are those in which some species terminate the reaction by

reacting with radicals, leading to a non-productive consumption of oxidant (Eqs. [1.8], [1.9]). Accordingly, these species are well known as radical scavengers.

Therefore, concentration of oxidant and catalyst must be selected in excess with respect to the stoichiometry, taking into account that an important amount of the reagents will end up in non-desirable reactions due to the presence of wide range of materials, such as soil organic matter, an excess of catalyst, some transition metals present in soil, etc.

Other important factors to consider for the application of Fenton's reagent are, on one hand, the loss of iron as a result of its precipitation when it is oxidized from Fe(II) to Fe(III) and the reaction pH is not enough acidic. On the other hand, the increase of temperature and formation of gases given that the reactions involved are exothermic as well as important amount of CO_2, O_2 may be released.

Therefore, although hydroxyl radicals are short-lived, conventional Fenton's reagent has been proved as an cost-effective technique for the removal of a great number of contaminants, such as diesel hydrocarbons (Kong et al., 1998; Watts and Teel, 2005), chlorinated compounds (Teel et al., 2001; Watts et al., 1990), explosives (Li et al., 1997; Matta et al., 2007), polycyclic aromatic hydrocarbons (Ferrarese et al., 2008; Flotron et al., 2005) and BTEX (Zhao et al., 2011).

1.3.3. Modified Fenton's reagent (MFR)

Although Modified Fenton's reagent is based on the Fenton's chemistry, the differentiating factor with respect to conventional Fenton's reagent lays in the presence of a specific additive, usually a chelating agent or hydrogen peroxide stabilizing agent.

According to this, Modified Fenton's reagent main objectives are focused on solving the main drawbacks derived from the application of conventional Fenton's reagent, such as the short half-life of hydroxyl radicals, the need of working under acidic conditions in order to avoid iron precipitation and the limitations of hydrogen peroxide transport due to its high reactivity (Vicente et al., 2011a). Accordingly, the addition of hydrogen peroxide stabilizers, like KH_2PO_4, which acts as radical scavenger, has been proved as an effective possibility which increases the extent of the remediation technique (Kakarla and Watts, 1997; Vicente et al., 2011a). On the other hand, the use

of chelating agents, such as sodium citrate, EDTA, has been more widely employed, since they can solve, or at least, minimize all drawbacks derived from conventional Fenton's reagent application. In this regard, the addition of a chelating agent lets the catalyst to be in aqueous solution for longer, can catalyze hydrogen peroxide under near neutral pH, increases its half-life, and thus minimizes the problems and risks derived from hydrogen peroxide transport (Rosas et al., 2014).

However, although the mechanisms of hydrogen peroxide activation by a complex iron-ligand are still quite unclear, the use of modified Fenton's reagent has been applied successfully for the treatment of soils under near neutral pH, without previous pH adjustment, contaminated by very different nature contaminants, such as polycyclic aromatic hydrocarbons (Venny et al., 2012), herbicides (Rosas et al., 2014) and gasolines (Watts et al., 2000).

1.3.4. Activated persulfate

Activated persulfate is, among ISCO techniques, one of the newest alternatives for the remediation of contaminated soils and groundwater. According to table 1.3, it can be seen that persulfate itself possess a high oxidation potential (2.1 V), and has the ability, as electrophilic specie (Eq. [12]) to degrade certain contaminants. Nevertheless, the most interesting application for environmental remediation in which persulfate is involved lies on the formation of the sulfate radical as a consequence of persulfate activation. In this sense, the high oxidation potential (2.6 V) of persulfate radicals makes these species degrade non-selectively a wide range of different organic pollutants, similarly to hydroxyl radical, and faster than persulfate anion.

Persulfate is normally applied in the form of sodium salt (Eq. [1.12]), given its higher solubility than potassium persulfate and its lower environmental impact than ammonium persulfate (Huling and Pivetz, 2006).

However, persulfate activation can be carried out by:

- Thermal or photo activation (Eq. [1.14])
- Activation with a transition metal (mainly by Fe^{2+}), Eq. [1.15]
- Activation under alkaline conditions (Eq. [1.16])
- Activation with hydrogen peroxide (Eq. [1.17])
- Activation with chelated metals

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \quad [1.12]$$

$$Na_2S_2O_8 \rightarrow 2Na^+ + S_2O_8^{2-} \quad [1.13]$$

$$S_2O_8{}^{2-} \xrightarrow{\text{heat or h}\nu} 2SO_4^{\cdot-} \quad [1.14]$$

$$S_2O_8{}^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot-} \quad [1.15]$$

$$S_2O_8^{2-} \xrightarrow{alkaline} SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot} \quad [1.16]$$

$$S_2O_8{}^{2-} + OH^{\cdot} \rightarrow SO_4^{2-} + SO_4^{\cdot} + \frac{1}{2}O_2 + H^+ \quad [1.17]$$

However, the complexity of the chemistry which involves the application of activated persulfate is due to not only sulfate radicals are formed during activation, but also hydroxyl radicals, are likely to appear under certain conditions (Siegrist et al., 2011).

On the other hand, although the formation of hydroxyl radicals may improve the extent of the remediation technique, it is important to point out that there are some termination reactions which, analogously to Fenton's reagent, decrease the effectiveness of the treatment. These termination reactions are related to the scavenging of sulfate or hydroxyl radicals, resulting in a non-productive consumption of persulfate. According to that, the most important scavenging reactions which may occur are:

- Scavenging by Fe(II) (Eq. [1.18])
- Scavenging by carbonate and/or bicarbonate
- Scavenging by chloride

$$SO_4^{\cdot-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \quad [1.18]$$

Therefore, according to Eq. [18], given that an excess of catalyst can result in an important grade of non-productive consumption of sulfate radicals, it has been proposed alternatives in order to solve this drawback, or at least, to minimize it. Therefore, it has been proposed to dose the catalyst in series instead of "at once" (Vicente et al., 2011b) as well as to use ZVI, which acts as a continuous release source of iron during treatment (Rodriguez et al., 2014). Although zerovalent iron does not activate persulfate directly,

it has been demonstrated that increases the effectiveness of sulfate radicals, as it extends the effective time of the oxidation and decreases non-productive consumption of sulfate radicals.

$$Fe^0 + S_2O_8{}^{2-} \rightarrow Fe^{2+} + SO_4^{2-} \qquad [1.19]$$

One last important point regarding persulfate activation is the fact that, sometimes it is useful to add Fe(III) salts for activation, mostly in cases when quinone type compounds (as oxidation by products or as components in soil humic acids) can be found in the matrix, and are able to reduce Fe(III) to Fe(II), hence working as a slow release source of Fe(II).

In conclusion, given the advantages of activated persulfate, such as its high persistence in soils (days to weeks), its high oxidation potential, its application appears as an attractive alternative to Fenton's reagent, ozone and permanganate. Nevertheless, there are still few scientific contributions in the literature regarding its application in real cases, which is probably its biggest drawback nowadays.

Despite the lack of real applications of activated persulfate, it has been arisen an increasing interest, reflected in the increasing number of research papers for the remediation of contaminated matrix (groundwater or soil) with activated persulfate, through a great number of different kind of activators and a wide range of different organic pollutants.

2.

OBJETO DEL TRABAJO
SCOPE AND GOALS

OBJETO DEL TRABAJO

El objeto de este trabajo se ha centrado en profundizar e incrementar el conocimiento sobre la aplicación del reactivo Fenton y persulfato activado para la eliminación de determinados contaminantes orgánicos persistentes de un suelo contaminado. En este sentido, se ha tratado el mismo tipo de suelo, correspondiente a un horizonte BT de un suelo del municipio de Arganda, en la Comunidad Autónoma de Madrid, contaminado artificialmente con diferentes tipos de compuestos. Se trata de un suelo neutro (pH = 7.22), con bajo contenido en materia orgánica (0.196%) y alto contenido en hierro (18200 $mg \cdot kg^{-1}$). El procedimiento de caracterización aparece en el trabajo de Vicente et al. 2012 *Diuron abatement in contaminated soil using Fenton-like process*. Chemical Engineering Journal 2012; 183: 357-364, y las propiedades de mayor relevancia están recogidas en la parte experimental de esta tesis.

Los contaminantes se han seleccionado por la facilidad con la que se pueden encontrar en suelos contaminados, como es el caso de gasolinas, diesel e hidrocarburos aromáticos policíclicos. El orden de tratamiento de dichos contaminantes ha sido en función a su persistencia en suelo, comenzando con - etilbenceno, siguiendo por las fracciones de hidrocarburos procedentes de biodiesel B20 y finalizando con hidrocarburos aromáticos policíclicos. En la Tabla 2.1 se muestran los contaminantes con los que se ha trabajado en el presente trabajo y su solubilidad aproximada en agua, cuyos datos han sido extraídos de la bibliografía.Para la eliminación de estos contaminantes, se han desarrollado distintos métodos cuyo objetivo es la aplicación del reactivo Fenton y el persulfato activado eficientemente. Los objetivos específicos quedan resumidos a continuación:

- Desarrollo de técnicas de análisis y de protocolos experimentales para la monitorización de las variables involucradas en la reacción y la determinación de las conversiones de los contaminantes. Dicho protocolo consta de las siguientes etapas:
    - Extracción de los contaminantes de su correspondiente matriz (ultrasonido para etilbenceno, Soxhlet para biodiesel y PAHs, y microondas para PAHs).

  - Análisis de los extractos orgánicos por cromatografía, de líquidos o gases.
  - Análisis de las fases acuosas (concentración de oxidante, pH, presencia de productos de oxidación, hierro en disolución, agente quelante, etc.)
- Eliminación de etilbenceno utilizando el reactivo Fenton:
  - Estudio de la influencia de las concentraciones de catalizador y oxidante en la evolución de las variables durante la reacción (consumo de oxidante, pH, concentración de quelante, concentración de catalizador y conversión de contaminantes).
  - Evaluación de las eficiencias de eliminación del contaminante, además de en términos de conversión, en términos de reducción de la toxicidad de la fase acuosa después del tratamiento.
- Eliminación de biodiesel B20 utilizando reactivo Fenton modificado y persulfato activado
  - Estudio de la eficiencia de eliminación de biodiesel B20, cuya persistencia es mayor que la del etilbenceno. Determinación de la influencia de diversas variables, como concentración de oxidante, concentración de catalizador/activador, concentración de contaminante en la evolución de oxidante, catalizador, quelante, concentración de contaminante en el suelo.
  - Evolución de las conversiones de cada una de las fracciones representativas del biodiesel, desde hidrocarburos alifáticos de 14 carbonos a 22.
  - Comparación de la ecotoxidad de la fase acuosa antes y después del tratamiento, con objeto de confirmar la ausencia de intermedios de oxidación más tóxicos que los contaminantes originales.
- Eliminación de PAHs utilizando reactivo Fenton y persulfato activado
  - Estudio de las conversiones de los diferentes PAHs en función de las condiciones de remediación (tipo de catalizador o activador, concentración, etc.)
  - Determinación de un modelo cinético de la remediación con persulfato activado que describa la evolución de la conversión de los contaminantes durante la aplicación de la técnica.

- Eliminación de PAHs utilizando persulfato activado inyectado en columna.
    - Simulación -de la- conversión -de los contaminantes con el tiempo de reacción a partir del modelo cinético obtenido de los experimentos realizados en discontinuo.
    - Estudio de los perfiles de concentración de contaminantes y de hierro a lo largo de la columna.

Tabla 2.1. Solubilidad y fórmula química de los contaminantes seleccionados en la presente tesis.

Contaminante		**Fórmula química**	**Soubilidad en agua ($mg \cdot L^{-1}$)**	**Ref.**
Compuestos de gasolinas	Etilbenceno	C_8H_{10}	180	(ATSDR, 2010)
Biodiesel tipo B20	~20% Ésteres metílicos de ácidos grasos	-	0.051 *predicho para (ester metílico del ácido linoleico)	*HMDB ALOGPS
	~80% Diesel de petróleo	-	~5 *valor medio	(Molina-Barahona et al., 2005)
Hidrocarburos aromáticos policíclicos	Antraceno Fenantreno Pireno Benzo(a)pireno	$C_{14}H_{10}$ $C_{14}H_{10}$ $C_{16}H_{10}$ $C_{20}H_{12}$	0.045 1.1 0.132 0.004	(Thompson and Nathanail, 2009)

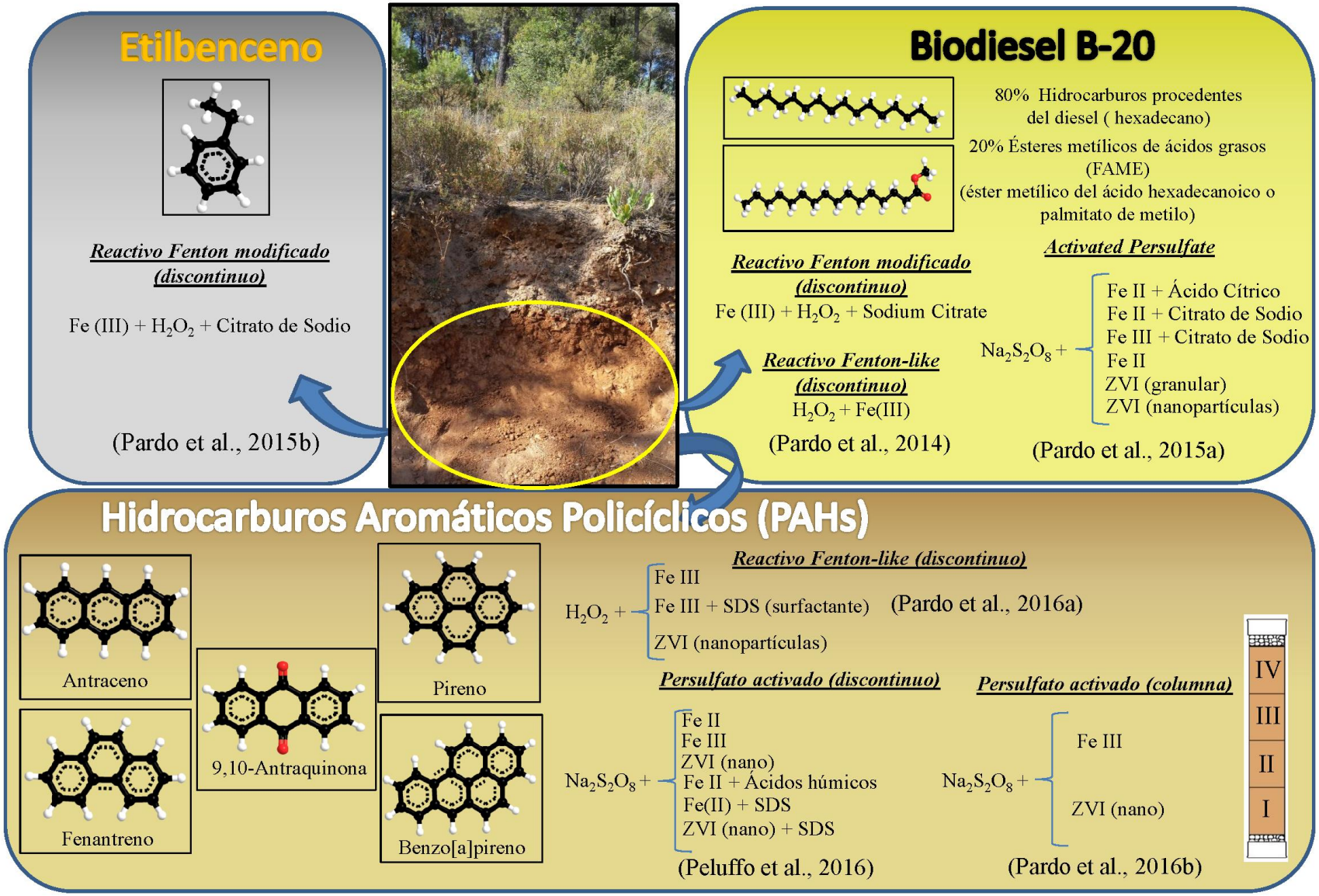

Fig. 2.1. Esquema gráfico de los tratamientos llevados a cabo.

SCOPE AND GOALS

The main objective of this Ph. D. thesis has been to expand knowledge in the application of Fenton's reagent and activated persulfate for the removal of persistent pollutants in contaminated soils. For this purpose, the same soil type, a sandy clay loam BT horizon from the Autonomous Community of Madrid, artificially spiked, has been used for all the studies. The soil selected has the following main properties; neutral pH (7.22), low organic matter content (0.196%) and high total iron content, measured from acid digestion (18200 $mg \cdot kg^{-1}$). Characterization procedure is detailed in the work by Vicente et al. 2012. *Diuron abatement in contaminated soil using Fenton-like process*. Chemical Engineering Journal 2012; 183: 357-364, and the most important properties are listed in the experimental section.

Selection of contaminants was based on the criteria of increasing persistence in soils and decreasing solubility in water- ethylbenzene, hydrocarbon fractions from B20 biodiesel blend and polycyclic aromatic hydrocarbons. In Table 2.1. are listed the contaminants of concern used in this thesis, besides, it is also shown their corresponding solubility in water, as reported in literature.

Table 2.1. Solubility and chemical formula of the selected contaminants used.

Contaminant		**Chemical formula**	**Solubility in water ($mg \cdot L^{-1}$)**	**Ref.**
Gasoline type compounds	Ethylbenzene	C_8H_{10}	180	(ATSDR, 2010)
Biodiesel B20 Blend	~20% Fatty acid methyl esters	-	0.051 *predicted for (linoleic acid methyl ester)	*HMDB ALOGPS
	~80% Petroleum diesel	-	~5 *average value	(Molina-Barahona et al., 2005)
Polycyclic Aromatic Hydrocarbons	Anthracene Phenanthrene Pyrene Benzo(a)pyrene	$C_{14}H_{10}$ $C_{14}H_{10}$ $C_{16}H_{10}$ $C_{20}H_{12}$	0.045 1.1 0.132 0.004	(Thompson and Nathanail, 2009)

For the removal of these pollutants, different methods to carry out Fenton's Reagent and activated persulfate have been performed. In this sense, the goals are summarized in the following points:

- Development of specific analysis techniques and experimental protocols for the monitoring of the variables involved during reaction as well as the correct determination of the removal efficiencies of the pollutants. Highlighting:
    - Extraction of contaminants from the soil matrix: (Ultrasound for ethylbenzene, Soxhlet for biodiesel blend and PAHs and Microwave extraction for PAHs).
    - Determination of organic species through gas and liquid chromatography.
    - Analysis of the aqueous phases (oxidant concentration, pH, presence of oxidation intermediates, iron in solution, chelating agent, etc.)
- Ethylbenzene removal by using Modified Fenton's reagent:
    - Find the better conditions through the study of the effect of catalyst and oxidant concentration on the evolution of the variables during reaction (oxidant consumption, pH, chelant concentration, catalyst concentration and contaminant conversion.
    - Find not only a satisfactory remediation technique in terms of contaminant removal but also in terms of toxicity reduction of the aqueous phase after treatments.
- Biodiesel B20 blend removal by using Modified Fenton's reagent and activated persulfate
    - Test the effectiveness of these techniques for the removal of pollutants with a more persistent nature than ethylbenzene. Study of the effect of several variables, such as oxidant, catalyst and pollutant concentration on the evolution of these variables with time, as well as the removal efficiency of the pollutant.
    - Evolution of the contaminants removal efficiency from the most representative fractions in biodiesel, on one hand the fatty acid methyl esters, and on the other the aliphatic hydrocarbons (from C14 to C22).

- Comparison of the ecotoxicity of the aqueous phase before and after treatment in order to confirm the presence or absence of toxic oxidation byproducts, in case of Modified Fenton's Reagent.

- PAHs removal by using Fenton's reagent and activated persulfate
  - Study the removal efficiency towards the different PAHs (3 ringed, 4 ringed and 5 ringed) as a function of the reaction conditions (type of catalyst, type of oxidant, catalyst concentration, etc.).
  - Under PS activation, carry out the development of a kinetic model in order to describe the consumption rate of the pollutants.
- PAHs removal by using activated persulfate in column
  - Estimate the contaminant conversions at the end of treatments from the kinetic models carried out in the remediation runs when PS was added in batch. Besides, to study the removal efficiency of pollutants along the column as well as the iron content.

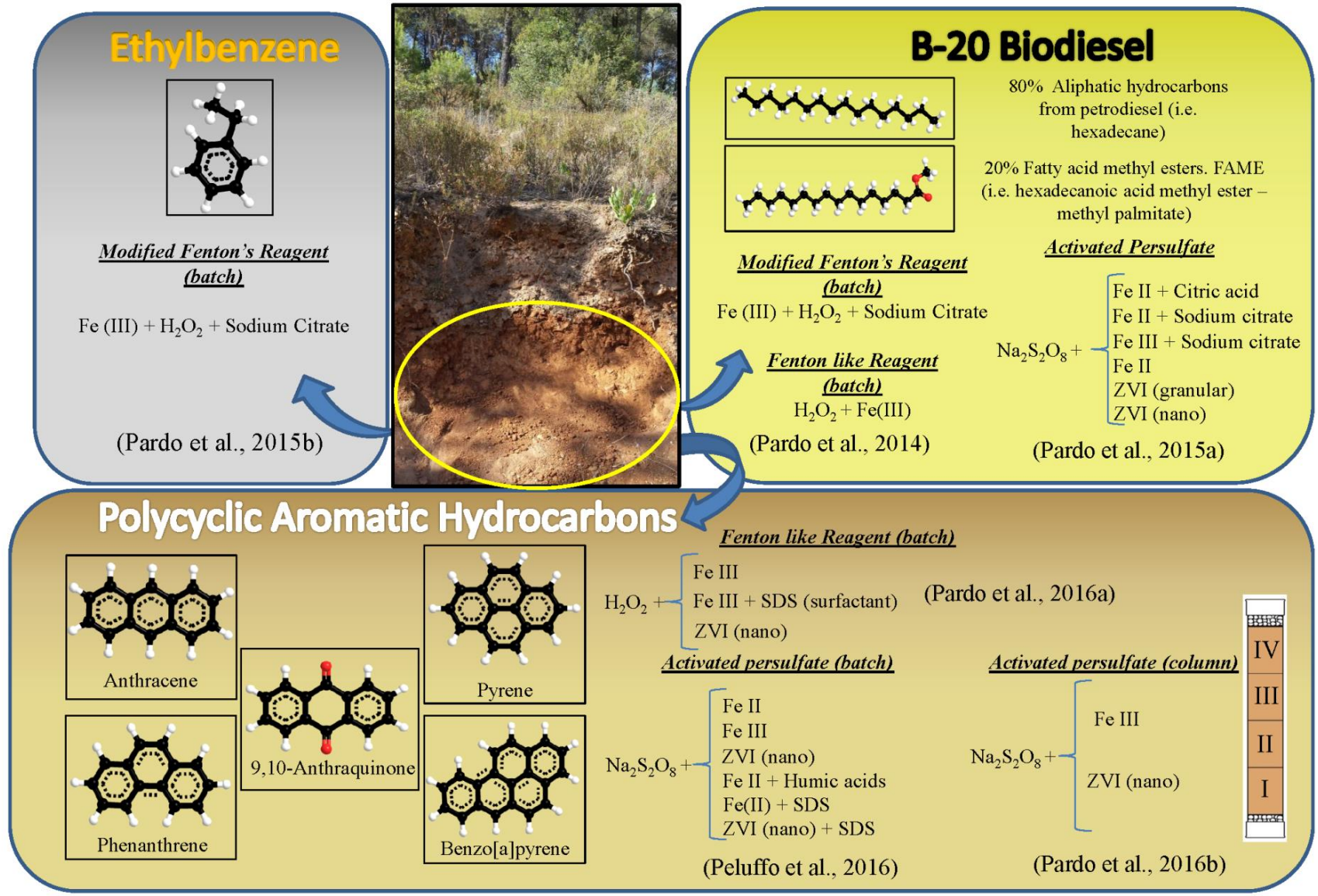

Fig. 2.1. Graphic overwiew of the treatments carried out

3.

DESARROLLO EXPERIMENTAL

En este capítulo se muestra el dispositivo experimental sobre el que se han realizado todos los tratamientos correspondientes a las publicaciones de la tesis, como son el suelo tratado, los reactivos utilizados, el procedimiento experimental, las técnicas de análisis y los equipos utilizados.

3.1. Materiales

3.1.1. Suelo

Las propiedades analizadas para la caracterización del suelo se muestran en la Tabla 3.1. En este apartado se describen los métodos de análisis de conductividad hidráulica, densidad aparente del suelo y capacidad de campo, el resto de parámetros están descritos en el trabajo de Vicente et al. 2012. La conductividad hidráulica fue determinada en el laboratorio de geodinámica del departamento de Hidrogeología y Medio Ambiente de la facultad de Ciencias Geológicas de la Universidad Complutense de Madrid. El suelo con el que se ha trabajado se caracteriza por tener un bajo contenido en materia orgánica (0.365%), alto contenido en hierro (18200 $mg \cdot kg^{-1}$) y pH neutro (7.22), propiedades de gran importancia en la aplicación de técnicas de oxidación química para la remediación de suelos, como son el reactivo Fenton y el persulfato activado.

La disponibilidad de hierro en el suelo afecta de manera muy importante a las técnicas de oxidación, ya que ciertos minerales férricos presentes en el suelo pueden catalizar el reactivo Fenton y también pueden actuar como fuente suministradora de hierro en el uso de persulfato activado (Ahmad et al., 2010; Kwan and Voelker, 2003), permitiendo reducir los costes derivados a la inyección de catalizador en la aplicación de estas técnicas en suelos reales.

El pH del suelo es neutro (pH = 7.22) y con muy bajo contenido en carbonatos (carbono inorgánico = 0.002 %), especies que afectan negativamente al desarrollo de técnicas de oxidación química por su papel como secuestradores de radicales hidroxilo (Huling et al., 1998).

El bajo contenido en materia orgánica (0.365%) se traduce en una disminución del consumo improductivo de oxidante. Esto se debe a que los radicales hidroxilo no son

selectivos y cuando se liberan pueden reaccionar indistintamente con el contaminante y con la materia orgánica presentes en el suelo, dándose un fenómeno competitivo entre dichas especies que afecta negativamente al proceso.

Tabla 3.1. Propiedades del suelo tratado en la presente tesis.

Textura del suelo		Franco arcillo arenoso
Materia orgánica del suelo (SOM) (%)		0.365
Carbono orgánico total (TOC) (%)		0.196
Fracciones de la materia orgánica (%)	**Fracción lábl I**	0.114
	Fracción lábil II	0.012
	Fracción recalcitrante	0.07
Carbono total (TC) (%)		0.198
Carbono inorgánico (IC) (%)		0.002
pH		7.22
Superficie BET ($m^2 \cdot g^{-1}$)		23
Volumen de poro de partícula ($cm^3 \cdot g^{-1}$)		0.031
Contenido en manganeso ($mg \cdot kg^{-1}$)		170
Contenido en hierro ($mg \cdot kg^{-1}$)	**Total**	18200
	Amorfo	525
	Cristalino	6710
Velocidad intersticial ($cm \cdot dia^{-1}$)		14.1
Densidad aparente del suelo ρ_L ($g \cdot cm^{-3}$)		1.445
Capacidad de campo (%)		49.0

Conductividad hidráulica y velocidad intersticial

La conductividad hidráulica o permeabilidad del suelo se midió utilizando un permeámetro (A = 0.05 m^2), proporcionado por Gomensoro, trabajando en condiciones de carga constante. Se introdujo el suelo hasta llenar el permeámetro (1.5 kg aproximadamente), se compactó y se anotó la longitud del lecho de suelo (Δl). Se midió la diferencia de potencial entre la entrada y salida de agua (Δh), se abrió el paso de agua y se midió el tiempo necesario hasta alcanzar un volumen determinado, calculando así el caudal (Q). La permeabilidad hidráulica (k) se calculó a partir de la aplicación de la ley de Darcy, según la Ec. [3.1],

$$k = \frac{Q}{A \cdot \frac{\Delta h}{\Delta l}} \qquad [3.1]$$

Además, la velocidad intersticial (u_l) de paso del agua en el suelo se calculó a partir de la porosidad del lecho (ε), según la Ec. [3.2]:

$$u_l = \frac{Q}{A \cdot \varepsilon} \qquad [3.2]$$

Fig. 3.1. Permeámetro de Gomensoro para la determinación de la permeabilidad del suelo.

Capacidad de campo

La capacidad de campo, definida como la cantidad de agua que un suelo es capaz de retener en condiciones de saturación, se determinó a partir del método de la columna de suelo. Se añadieron 20 g de suelo en un embudo de vidrio con papel de filtro, colocado en la parte superior de una probeta. Posteriormente se añadieron lentamente 40 mL de agua y se dejó filtrar durante 24 horas. El agua retenida en el suelo se calculó por diferencia entre el agua total introducida y el agua que pasó filtrada a la probeta. Este dato también se verificó por diferencia de pesada del suelo antes y después de incorporar el agua. A partir del agua retenida se calculó la capacidad de campo del suelo (Ec. [3.3]).

$$\%\ Capacidad\ de\ campo = \frac{w_{agua}}{w_{suelo\ seco}} \qquad [3.3]$$

Densidad aparente

La densidad aparente (ρ_L), expresada como la masa total de partículas sólidas respecto a su volumen total, se midió llenando una probeta de precisión con suelo hasta alcanzar 100 mL. Posteriormente se pesó el suelo y se secó en estufa (Memmert,

modelo UFE 400) a 105ºC durante 24 h. Por último, se volvió a pesar el suelo seco. En la Ec. [3.4] se muestra el cálculo de la densidad aparente:

$$\rho_L\ (g \cdot cm^{-3}) = \frac{masa\ suelo\ seco}{volumen\ de\ suelo} \qquad [3.4]$$

3.1.2. Reactivos

En la Tabla 3.2 se muestran los reactivos utilizados en los diferentes tratamientos de remediación, indicándose CAS, grado de pureza, proveedor, fórmula molecular y aplicación, y por otro, en la Tabla 3.3, los reactivos utilizados en los métodos analíticos.

Tanto en los tratamientos de remediación como en los métodos de análisis se ha utilizado agua Milli-Q, con una resistividad máxima de 18.2 μΩ·cm, obtenida de un equipo Direct-8 de Millipore.

Tabla 3.2. Reactivos usados en los tratamientos.

CAS	*Reactivo*	*Formula química*	*Pureza*	*Proveedor*	*Finalidad*
100-41-4	Etilbenceno	C_8H_{10}	99%	Sigma – Aldrich	Contaminante
-	Biodiesel B20	-	-	Shell	Contaminante
120-12-7	Antraceno	$C_{14}H_{10}$	99%	Aldrich	Contaminante
85-01-8	Fenantreno	$C_{14}H_{10}$	≥ 96%	Sigma-Aldrich	Contaminante
129-00-0	Pireno	$C_{16}H_{10}$	98%	Aldrich	Contaminante
50-32-8	Benzo(a)pireno	$C_{20}H_{12}$	≥ 96%	Aldrich	Contaminante
7722-84-1	Peróxido de hidrógeno	H_2O_2	≥ 30%	Fisher Chemical	Oxidante
			≥ 35%	Sigma – Aldrich	
7775-27-1	Persulfato de sodio	$Na_2S_2O_8$	≥ 98%	Sigma – Aldrich	Oxidante
10028-22-5	Sulfato férrico x-hidratado	$Fe_2(SO_4)_3 \cdot nH_2O$	75%	Panreac	Catalizador

Tabla 3.2. Reactivos usados en los tratamientos (continuación).

CAS	*Reactivo*	*Formula química*	*Pureza*	*Proveedor*	*Finalidad*
7782-63-0	Sulfato ferroso heptahidratado	$Fe(SO_4)\cdot 7H_2O$	≥ 99%	Fisher Chemical	Activador
-	Nanopartículas de hierro cerovalente (partículas estabilizadas)	Fe	≥ 92%	NANOIRON	Activador
151-21-3	Dodecil sulfato de sodio	$C_{12}H_{25}NaO_4S$	> 99%	Sigma – Aldrich	Surfactante
10102-17-7	Tiosulfato de sodio pentahidratado	$Na_2S_2O_3\cdot 5H_2O$	≥ 99.5%	Sigma – Aldrich	Parada de la reacción de persulfato
7439-89-6	Partículas de hierro cerovalente granular	Fe	≥ 99.5%	Sigma	Activador
77-92-9	Ácido cítrico	$C_6H_8O_7$	≥ 99.5%	Panreac	Agente quelante
68131-04-4	Sales sódicas de ácidos húmicos	-	45 – 70%	Acros Organics	Aditivo activación persulfato
67-56-1	Metanol	CH_4O	99.9 % (grado HPLC)	Fisher Chemical	Parada de la reacción Fenton

Tabla 3.3. Reactivos usados en las técnicas de análisis.

CAS	*Reactivo*	*Formula química*	*Pureza*	*Proveedor*	*Finalidad*
7664-93-9	Ácido sulfúrico	H_2SO_4	> 95%	Fisher Chemical	Análisis de peróxido
7722-64-7	Permanganato potásico	$KMnO_4$	99.5%	Panreac	Análisis de peróxido
75-05-8	Acetonitrilo	C_2H_3N	99.9% (grado HPLC)	Fisher Chemical	Eluyente de HPLC (etilbenceno)
67-56-1	Metanol	CH_4O	99.9 % (grado HPLC)	Fisher Chemical	Extracción de etilbenceno

Tabla 3.3. Reactivos usados en las técnicas de análisis. (continuación)

CAS	*Reactivo*	*Formula química*	*Pureza*	*Proveedor*	*Finalidad*
7697-37-2	Ácido nítrico	HNO_3	69.5%	Scharlau	Análisis de metales
7664-38-2	Ácido fosfórico	H_3PO_4	≥ 85%	Sigma Aldrich	Eluyente de HPLC (citrato)
7778-77-0	Fosfato de potasio monobásico	KH_2PO_4	≥ 99.5%	Sigma Aldrich	Eluyente de HPLC (citrato)
6153-56-6	Ácido oxálico dihidratado	$C_2H_2O_4 \cdot 2H_2O$	≥ 99.5%	Merck	Patrón análisis
141-82-2	Ácido malónico	$C_3H_4O_4$	99%	Merck	Patrón análisis
328-50-7	Ácido 3-oxoglutárico	$C_5H_6O_5$	99%	Aldrich	Patrón análisis
10102-17-7	Tiosulfato de sodio pentahidratado	$Na_2S_2O_3 \cdot 5H_2O$	≥ 99.5%	Sigma – Aldrich	Valoración de persulfato
7681-11-0	Ioduro de potasio	KI	> 99.5%	Fisher Chemical	Valoración de persulfato
7757-82-6	Sulfato de sodio anhidro	Na_2SO_4	99%	Fisher Chemical	Secado muestras suelo
67-64-1	Acetona	C_3H_6O	99.8% (grado HPLC)	Fisher Chemical	Extracción muestras biodiesel y PAHs
110-54-3	n-hexano	C_6H_{14}	99% (grado HPLC)	Scharlab	
75-09-2	Diclorometano	CH_2Cl_2	99.8% (grado HPLC)	Sigma – Aldrich	
497-19-8	Carbonato sódico	Na_2CO_3	99.8%	Panreac	Análisis de ácidos orgánicos (cromatografía iónica)
144-55-8	Bicarbonato sódico	$NaHCO_3$	99.7%	Panreac	Análisis de ácidos orgánicos (cromatografía iónica) Valoración de persulfato

3.2. Procedimiento experimental y equipos

En este apartado se realiza una breve descripción de las diferentes etapas que se han llevado a cabo durante el procedimiento experimental que aparece descrito en cada una de las publicaciones de la presente tesis. Estas etapas son el consumo improductivo de oxidante en el suelo, la contaminación del suelo y los tratamientos de remediación.

3.2.1. Consumo improductivo de oxidante

La presencia de especies reductoras en el suelo, como metales de transición, y de la materia orgánica del suelo, afecta a la eficiencia de las técnicas de oxidación química, dando lugar a un consumo improductivo de oxidante (Romero et al., 2009), que debe ser tenido en cuenta. Por ello, previamente a los tratamientos de remediación, se estudió el consumo improductivo de oxidante (peróxido de hidrógeno y persulfato) en el suelo en condiciones similares a las de los experimentos de remediación.

Para ello, se llevaron a cabo una serie de experimentos en discontinuo (*batch*), utilizando tubos de centrífuga de politetrafluoroetileno (PTFE) de 50 mL (Figura 3.2), agitados en baño orbital termostatizado a 20ºC (SW22 de Julabo y *Unitronic Orbital* de Selecta, Figura 3.3) en los que se añadieron 10 mL de disolución acuosa con cierta cantidad de oxidante (100 y 200 mmol·L^{-1} de persulfato, 882 y 2000 mmol·L^{-1} de peróxido de hidrógeno) en 5 g de suelo sin contaminar, siendo la relación fase acuosa:suelo de 2 mL·g^{-1}.

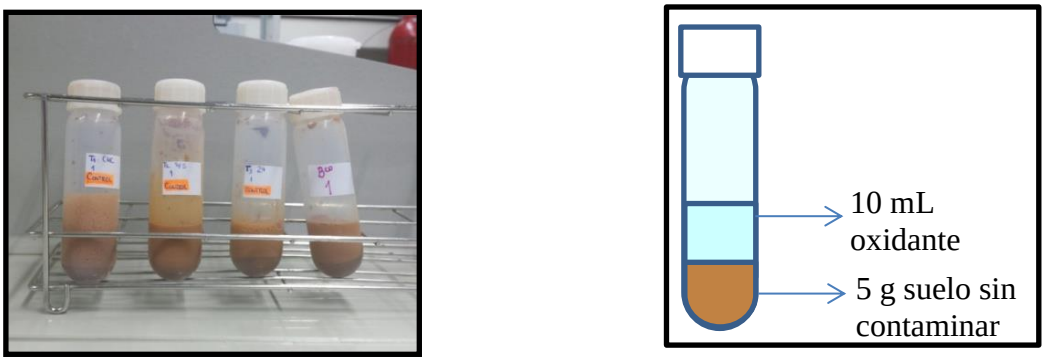

Fig. 3.2. Tubos de PTFE utilizados para los experimentos en discontinuo.

Fig. 3.3. Equipos de agitación utilizados para los ensayos en discontinuo. Izquierda: Julabo SW 22, derecha: Unitronic Orbital de Selecta.

3.2.3. Contaminación de las muestras

Etilbenceno

Las muestras de suelo contaminado con etilbenceno se prepararon añadiendo el contaminante puro con una pipeta sobre los 5 g de suelo limpio. Las cantidades añadidas variaron dependiendo de la concentración deseada, entre 9.4 y 188 $mmol_{EB} \cdot kg_{suelo}^{-1}$. La contaminación de las muestras acuosas se realizó pipeteando la cantidad deseada (0.094 o 0.94 $mmol_{EB}$) de etilbenceno en 10 mL de disolución acuosa con agente quelante y catalizador, sulfato férrico. Se estableció como tiempo cero de la reacción el momento en que se añadió el peróxido de hidrógeno

Biodiesel B20

La contaminación del suelo con biodiesel B20, previa caracterización de las distintas fracciones de hidrocarburos presentes, como se muestra en la Figura 3.4, se realizó añadiendo 500 mL de una disolución de 2000 y 20000 $mg \cdot L^{-1}$ del contaminante en n-hexano con objeto de alcanzar 1000 y 10000 $mg \cdot kg^{-1}$, respectivamente. La muestra se llevó a agitación en baño a 20ºC durante 24 horas y posteriormente se dejó evaporar el disolvente en campana extractora durante 48 horas.

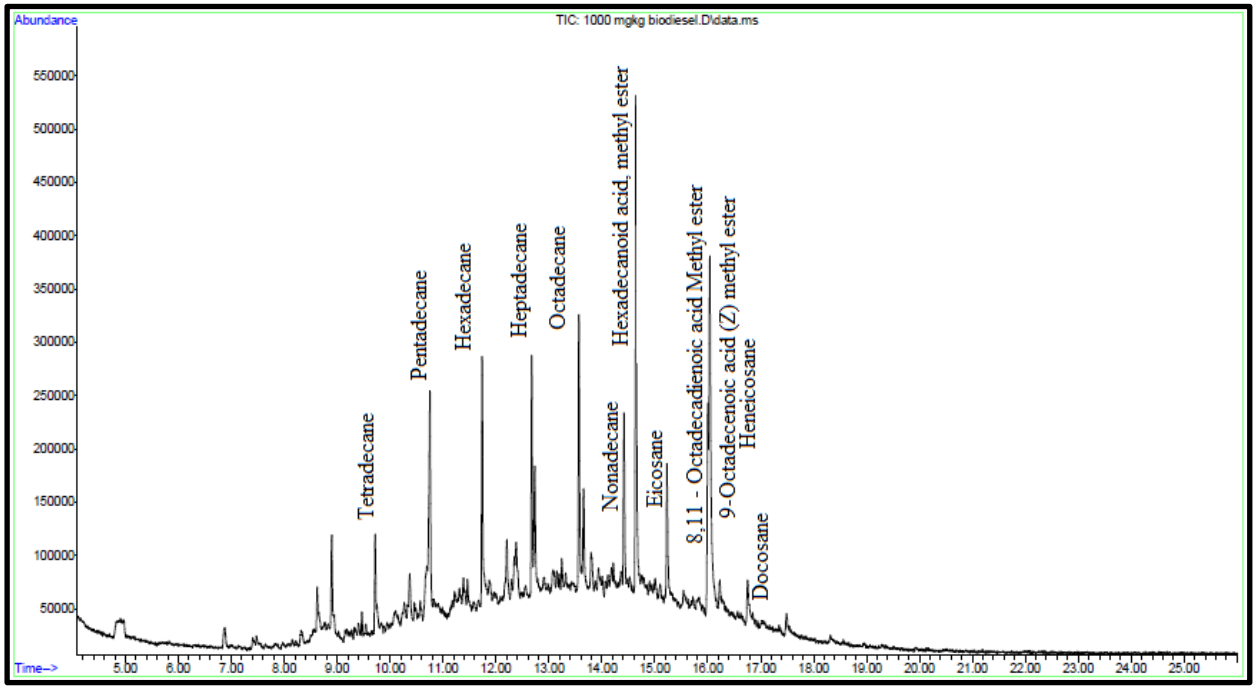

Fig. 3.4. Cromatograma representativo de una muestra de biodiesel B20 en nhexano:acetona tras extracción de un suelo antes de ser tratado.

Hidrocarburos poliaromáticos

Para contaminar el suelo con hidrocarburos poliaromáticos se preparó una disolución con 60 mg de cada uno de los contaminantes, fenantreno, antraceno, pireno y benzo(a)pireno en 50 mL de acetona. Esta disolución se dosificó con pipeta lentamente sobre 600 mg de suelo mientras se iba removiendo con una espátula. Este procedimiento de contaminación permite minimizar el impacto del disolvente en las comunidades microbianas del suelo (Mora et al., 2014).

Los tratamientos en discontinuo se realizaron inmediatamente después de contaminar el suelo, sin embargo, los tratamientos en discontinuo se pusieron en marcha después de un periodo de envejecimiento de 3 meses del suelo tras ser contaminado.

3.2.4. Tratamientos de remediación

A lo largo de la experimentación, los tratamientos se llevaron a cabo de dos maneras, en discontinuo (batch) y en continuo. Los experimentos en un sistema en discontinuo tienen gran utilidad como ensayos preliminares por aportar información valiosa sobre la efectividad entre unos tratamientos y otros y por su sencillez, ya que además permiten la realización de varios experimentos al mismo tiempo. Los

experimentos en continuo, a su vez, permiten acercar las condiciones experimentales a las de un caso real al tenerse en cuenta los aspectos hidrodinámicos del suelo.

El procedimiento de los tratamientos en discontinuo se realizó de manera análoga a los experimentos de consumo improductivo, llevando a cabo las reacciones en tubos de PTFE de centrífuga de 50 mL en baño orbital termostatizado, operando en modo isotermo a 20 ºC y sin ajuste previo del pH del medio. Cada tubo de centrífuga representaba un tiempo determinado de reacción, por lo que se sacrificaba completamente al tiempo seleccionado, se paraba la reacción (metanol en caso de peróxido de hidrógeno y tiosulfato de sodio en caso del persulfato) y se analizaban los parámetros correspondientes (concentración de oxidante, de contaminante, pH, hierro total en disolución, agente quelante).

Los tratamientos en continuo se realizaron en la aplicación de persulfato activado para la eliminación de hidrocarburos poliaromáticos con objeto de aproximar las condiciones experimentales a las de un caso real, trabajando a velocidades de flujo cercanas a la velocidad de infiltración del agua en la zona saturada del suelo.

A continuación se describen las etapas seguidas en cada uno de los siguientes tipos de tratamientos.

Tratamientos en discontinuo

Eliminación de etilbenceno por reactivo Fenton modificado

En la eliminación de etilbenceno con reactivo Fenton modificado se llevaron a cabo dos tipos de reacciones, en fase líquida y en suelo. Las etapas seguidas durante las reacciones fueron las siguientes:

1. Puesta en marcha de la reacción, introduciendo en el baño agitado los tubos de reacción por duplicado para cada tiempo de reacción (24, 48, 72, 96 y 120 horas), además de un tubo de control para medir el pH del medio (72 horas) y cuatro adicionales, correspondiendo con los tiempos finales tras comprobar el consumo total de oxidante, con objeto de analizar el carbono orgánico total y la ecotoxicidad.

2. Para tiempos intermedios, los tubos seleccionados se enfriaron a -18ºC para minimizar las pérdidas por volatilización y se añadieron 15 mL de metanol, especie que actúa como secuestrador de radicales (Ko et al., 2012), para detener la reacción.

   - Reacciones con suelo: La adición de metanol fue seguida de sonicación durante 1 hora en baño de ultrasonidos en un equipo Powersonic 505 (Figura 3.5). Posteriormente las muestras se centrifugaron en un equipo Meditronic-BL de Selecta (Figura 3.6), durante 10 minutos a 10000 rpm y se separaron las fases líquida y el suelo. En esta etapa se comprobó la ausencia de etilbenceno retenido en el suelo tras la extracción.
   - Reacciones en fase líquida: agitación de la muestra para homogeneizar las fases.

3. Análisis de peróxido de hidrógeno, etilbenceno, hierro en disolución, citrato e intermedios de reacción de la muestra.

   - Cuantificación del peróxido de hidrógeno tomando 50 μL de muestra y valorándolas por titración potenciométrica.
   - Se tomaron 0.1 mL de muestra, a los que se añadieron 0.9 mL de metanol para analizar la concentración de etilbenceno por HPLC.
   - Se tomaron otros 0.1 mL de muestra, que se mezclaron con 0.9 mL de una disolución tampón de KH_2PO_4 20 $mmol \cdot L^{-1}$y se analizó el citrato remanente e intermedios de oxidación por HPLC.
   - Se tomaron 5 mL de muestra y se analizó la presencia de intermedios de oxidación, de manera complementaria al análisis por HPLC.
   - Se tomó 1 mL de muestra, se añadieron 9 mL de agua Milli-Q y se acidificó con HNO_3 a una concentración de 1% en volumen y se analizó el hierro total en disolución por espectrometría de emisión atómica inducida por microondas (MP-AES).

Fig. 3.5. Baño de ultrasonidos Powersonic 505.

4. Para los tiempos finales, tras asegurar la ausencia de peróxido de hidrógeno remanente en el medio, y sin adición de metanol:

   - Se tomaron 3 mL de muestra a los que se añadieron 12 mL de agua MilliQ y se acidificaron con ácido fosfórico, para eliminar el carbono inorgánico, con objeto de analizar el carbono orgánico total en disolución.
   - Se tomaron los 10 mL de uno de los tubos y se analizó la toxicidad siguiendo el procedimiento estándar del test Microtox.

Fig. 3.6. Centrífuga Meditronic-BL de Selecta.

Eliminación de biodiesel B20 por reactivo Fenton modificado y persulfato activado

En la aplicación del reactivo Fenton modificado y de persulfato activado para la remediación de suelo contaminado con biodiesel B20 se siguieron las mismas etapas. La

única diferencia radicó en el análisis de oxidante, que fue peróxido de hidrógeno en un caso y persulfato en el otro.

1. Se introdujeron en el baño agitado los tubos, representando cada dos tubos un tiempo de reacción, y 4 adicionales reservados para el tiempo final, con objeto de analizar el carbono orgánico total de la fase acuosa y la toxicidad de la fase acuosa muestra.
2. Para los tiempos de reacción seleccionados, se añadieron 10 mL de una mezcla de n-hexano y diclorometano, al 50% cada uno de ellos en volumen, sobre el medio de reacción.
3. Se centrifugó toda la mezcla, observándose tres fases diferenciadas, la fase acuosa en la parte superior, la fase orgánica en el medio y el suelo en la parte inferior, como se muestra en la Figura 3.7.

Fig. 3.7. Ejemplo de muestra de reacción tras adición de 10 mL de nhexano:diclorometano 1:1 y centrifugación.

4. Se midió el pH de la fase acuosa y se añadieron 5 mL de metanol para detener la reacción. De la muestra resultante se analizaron el peróxido de hidrógeno o el persulfato, según correspondiese (50 μL de muestra en cada caso), el agente quelante (citrato de sodio o ácido cítrico) y el hierro total en disolución remanentes, utilizando las mismas cantidades de muestra que las descritas anteriormente.

5. La fase orgánica se analizó por GC-FID para cuantificar el contenido de TPH.

6. El suelo húmedo se mezcló con sulfato de sodio hasta obtener un polvo seco, el cual se extrajo con una mezcla de n-hexano:acetona 1:1 en un extractor Soxhlet (Figura 3.8) siguiendo el método 3540C de la EPA (USEPA, 1996). El extracto obtenido se analizó por GC-FID para cuantificar el contenido en TPH y por GC-MS para identificar las distintas fracciones de hidrocarburos remanentes.

Fig. 3.8. Extractores Soxhlet utilizados para la extracción de los contaminantes remanentes en el suelo.

Eliminación de hidrocarburos poliaromáticos

1. Las reacciones se realizaron por duplicado, y además se añadió un tubo adicional de reacción, que servía de control, en el que se analizaba oxidante remanente cada 24 horas para sacrificar los tubos correspondientes a tiempos de reacción en los que la concentración era de un 0, 25, 50 y 75% respecto de la inicial. El tiempo final de reacción fue de 40 días para los ensayos con peróxido de hidrógeno y de 50 para los ensayos con persulfato.

2. Los tubos de reacción sacrificados se centrifugaban (Meditronic-BL de Selecta) durante 10 minutos a 10000 rpm y se separaba la fase acuosa del suelo.

3. De la fase acuosa se analizaron pH, concentración de peróxido de hidrógeno o persulfato, concentración de hierro total en disolución. Posteriormente, se realizó una extracción de dicha fase acuosa, añadiendo 10 mL de n-hexano. Del extracto orgánico se analizó el contenido de hidrocarburos poliaromáticos por HPLC.

4. El suelo fue tratado de manera análoga a los experimentos de eliminación de biodiesel B20, mezclando sulfato de sodio con el suelo húmedo hasta obtener un polvo seco que se extraía posteriormente con 50 mL de una mezcla orgánica de nhexano:acetona 1:1 en Soxhlet. Dicho extracto se analizó por HPLC para cuantificar los hidrocarburos poliaromáticos remanentes en suelo.

5. Para la detección de intermedios de oxidación, se tomaron 20 mL de los extractos orgánicos y se evaporaron a temperatura ambiente en una campana extractora, para

posteriormente ser reconstituidos con 2 mL de diclorometano y analizados por GC-MS.

Tratamientos en continuo

Los experimentos en continuo se realizaron en columna en flujo ascendente, con la ayuda de una bomba peristáltica (modelo Spetec de Perimax) para asegurar en todo momento condiciones de saturación. Las propiedades de la columna y los parámetros de flujo se resumen en la Tabla 3.4 y en la Figura 3.9 se muestra una de las columnas con las que se trabajó, al comienzo del tratamiento, durante el llenado con agua MilliQ.

Tabla 3.4. Parámetros de flujo y características de la columna en los tratamientos de remediación llevados a cabo en continuo.

Diámetro de la columna	3 cm
Longitud de la columna	24.6 cm
Cantidad de suelo	150 g
Longitud del tramo de suelo	17.5 cm
Diámetro esferas de vidrio	1 mm
Longitud tramo esferas de vidrio	1.5 cm
Densidad aparente del suelo	1.445 $g \cdot cm^{-1}$
Caudal de entrada	43.2 $cm^3 \cdot dia^{-1}$
Velocidad intersticial	13.9 $cm \cdot dia^{-1}$
Volumen de poro del suelo	74 cm^3
Porosidad del suelo	0.43

Los experimentos de remediación se llevaron a cabo durante 25 días bajo las siguientes condiciones:

1. Blanco: Se introdujo agua MilliQ durante 25 días.
2. Control: Se inyectó persulfato solamente con objeto de evaluar la capacidad de activación del hierro presente en el suelo.
3. Activación con Fe(III): Se inyectaron dos disoluciones simultáneamente, una de sulfato férrico 1 $mmol \cdot L^{-1}$ de Fe(III) y otra de persulfato sódico 200 $mmol \cdot L^{-1}$.
4. Activación con nanopartículas de hierro cerovalente: Se inyectó primeramente una suspensión con nanopartículas de hierro, procedente de un recipiente agitado al que se burbujeaba nitrógeno para minimizar la oxidación del hierro cerovalente. Tras alcanzar la cantidad deseada de hierro dentro de la columna se inyectó el persulfato durante 25 días.

En las Figuras 3.10 y 3.11 se muestran los esquemas de las instalaciones experimentales correspondientes a la activación del persulfato con Fe(III) y nanopartículas de hierro, respectivamente.

Fig. 3.9. Foto de una de las columnas al comienzo del tratamiento, durante el llenado previo con agua MilliQ.

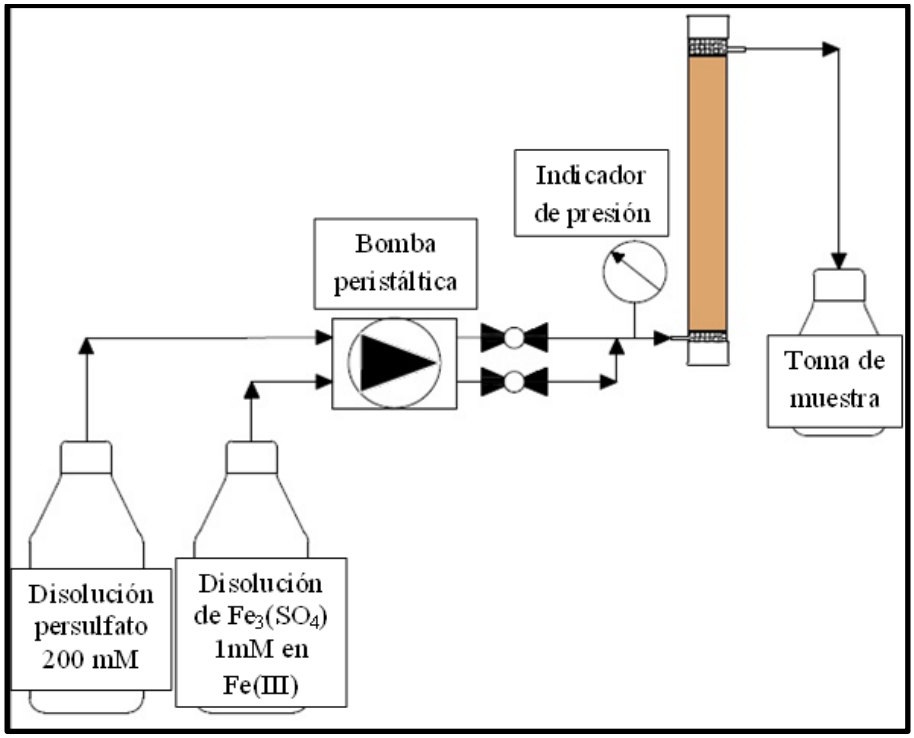

Fig. 3.10. Esquema de la instalación experimental en la que se inyectaron simultáneamente persulfato de sodio 200 mmol·L^{-1} y sulfato férrico ($C_{Fe(III)0}$=1 mmol·L^{-1})

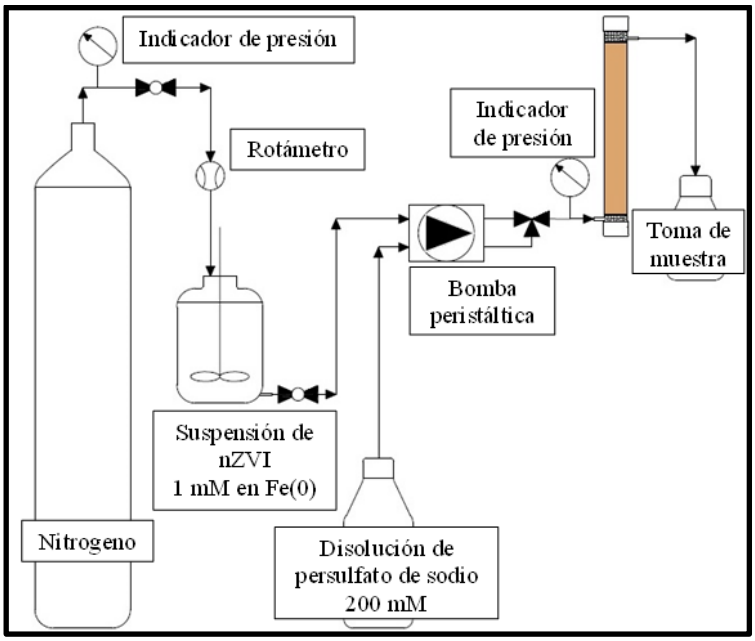

Fig. 3.11. Esquema de la instalación experimental en la que se inyectaron inicialmente las nanopartículas de hierro cerovalente (C_{Fe0}=1 y C_{Fe0}=896 mmol·L^{-1}) y posteriormente se inyectó el persulfato (C_{PS0}=200 mmol·L^{-1}).

Durante los tratamientos, se tomaron muestras a la salida de la columna diariamente, de las que se analizaron la concentración de persulfato por titración potenciométrica, el pH y la concentración del hierro en disolución por colorimetría o por MP-AES. Además, se realizó extracción líquido-líquido con n-hexano, y tras agitación durante 4 horas, el extracto líquido orgánico se filtró y analizó por HPLC para verificar la presencia de hidrocarburos poliaromáticos en el efluente.

Transcurridos los 25 días de reacción, el suelo se retiró de la columna y se dividió en cuatro secciones de similar peso en suelo mojado. A dichas muestras se añadieron 15 mL de tiosulfato sódico 400 mmol·L^{-1} para parar la reacción, y la cantidad necesaria de sulfato de sodio anhidro hasta obtener un polvo seco. Se determinó el contenido de humedad de las distintas secciones de suelo retirando 10 g de suelo mojado y secándolas a 105ºC durante una hora. Además 2g de ese suelo seco fueron llevados a extracción con 20 mL de EDTA para cuantificar el hierro lábil extractable con agente quelante, que se midió por colorimetría.

En los experimentos con adición de nanopartículas de hierro se realizaron además extracción ácida con HNO_3 de las secciones de esferas, para verificar la cantidad de hierro retenido en dichas secciones.

El contenido en hidrocarburos poliaromáticos se realizó por extracción con nhexano:acetona 1:1 de las muestras secadas y trituradas en mortero en un equipo de microondas ETHOS ONE, de Milestone (Figura 3.12). Los extractos orgánicos se filtraron y se analizaron por HPLC.

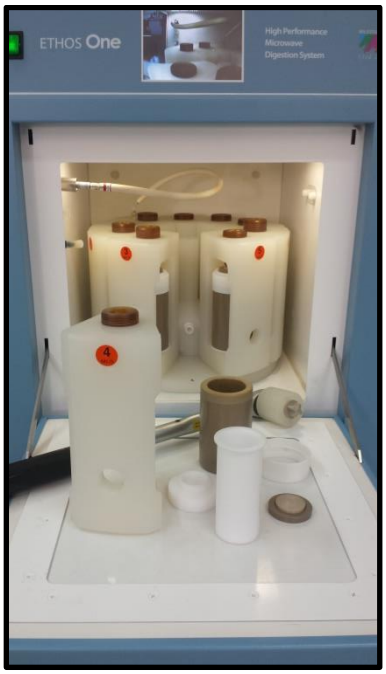

Fig. 3.12. Extractor microondas ETHOS ONE, de Milestone.

3.3. Métodos de análisis

En la Tabla 3.5 se muestran las diferentes técnicas de análisis utilizadas a lo largo del procedimiento experimental. Además, se muestran de manera resumida

Tabla 3.5. Técnicas de análisis utilizadas y condiciones

Técnica de análisis	Equipo	Finalidad	Acondicionamiento de muestras	Agente valorante
Titración potenciométrica	Módulo titración Metrohm 905-1 Con electrodo de Pt especial Redox	Cuantificación de peróxido de hidrógeno	· Se diluyen 50µL de muestra en 50 mL de una disolución de H_2SO_4 10% en volumen. · Se valora la muestra resultante.	$KMnO_4$ 5 mmol·L^{-1}
		Cuantificación de persulfato	· Se diluyen 50 µL de muestra, 4 g de KI y 0.2 g de $NaHCO_3$ en 50 mL de agua Milli-Q. · Se deja reaccionar la mezcla durante 15 minutos · Se acidifica el medio con 1 mL de ácido acético 6 mol·L^{-1} · Se valora la muestra resultante	$Na_2S_2O_3$ 300 mg·L^{-1}

Técnica de análisis	Equipo	Finalidad	Acondicionamiento de muestras	Velocidad inyección muestra	Nebulizador	Longitud de Onda Fe
MP-AES	MP-AES 4100 de Agilent	Cuantificación de Fe total en disolución.	· Las muestras se acidifican con HNO_3 (1% en volumen)	8 rpm	OneNeb	259.94 nm

Técnica de análisis	Equipo	Finalidad	Columna	Fase móvil	Caudal	Volumen inyección	Temperatura	Longitudes de onda
HPLC	HPLC Agilent, modelo 1100 Detector Agilent 1290 DAD	Análisis de etilbenceno	Chromolith RP-18e 100 x 4.6 mm	70 % Acetonitrilo 30% Agua Milli-Q	0.2 mL·min^{-1}	5 µL	40 ºC	Etilbenceno 208 nm
		Análisis de citrato		Disolución tampón 20 mmol·L^{-1} KH_2PO_4 pH = 2.1 (H_3PO_4)	0.2 mL·min^{-1}	5 µL	20 ºC	Citrato 210 nm
		Análisis de PAH	Poroshell 120 SB-C18 2.1 mm x 100 mm x 2.7 µm	60% Acetonitrilo 40% Disolución tampón 70 mmol·L^{-1} KH_2PO_4	0.5 mL·min^{-1}	20 µL	20 ºC	Antraceno 250 nm Fenantreno 250 nm Pireno 235 nm Benzo(a)pireno 295 nm

Tabla 3.5. Técnicas de análisis utilizadss y condiciones (continuación)

Técnica de análisis	Equipo	Finalidad	Columna	Fase móvil	Caudal	Volumen inyección	Temperatura
Cromatografía iónica	Modelo 761Metrohm	Análisis productos oxidación citrato	Metrosep A supp10	$NaHCO_3$ y Na_2CO_3 5 mmol·L^{-1} cada uno	1 mL·min^{-1}	20 µL	20ºC

Técnica de análisis	Equipo	Finalidad	Columna	Gas portador	Caudal	Condiciones de inyección	Temperatura del detector	Programa de temperatura del horno
GC-FID	GC – FID (HP 6890)	Cuantificación TPH en biodiesel B20	Capilar DB – 1 30m x 0.25mm x 1µm	He (pureza 99.9992%)	10 mL·min^{-1}	Volumen: 5 µL Splitless Tª = 280 ºC	330 ºC H_2 y N_2 (purezas ≥ 99.9992%)	Temperatura inicial 45 ºC 1ª Rampa 12 ºC·min^{-1} hasta 250 ºC 2ª Rampa 8ºC·min^{-1} hasta 325 ºC
GC-MS	GC – MS (HP 6890N, MSD 5975B)	Análisis fracciones de biodiesel B20	Capilar HP – 5 30m x 0.32mm x 0.25µm	He (pureza 99.9992%)	10 mL·min^{-1}	Volumen: 5 µL Splitless Tª = 280 ºC	-	Temperatura inicial 45 ºC 1ª Rampa 12 ºC·min^{-1} hasta 250 ºC 2ª Rampa 8ºC·min^{-1} hasta 325 ºC
		Análisis intermedios de oxidación PAH			2 mL·min^{-1}	Volumen: 8 µL Splitless Tª = 280 ºC		Temperatura inicial 45 ºC 1ª Rampa 5 ºC·min^{-1} hasta 150 ºC 2ª Rampa 8ºC·min^{-1} hasta 325 ºC

Tabla 3.5. Técnicas de análisis utilizadas y condiciones (continuación)

Técnica de análisis	Equipo	Finalidad	Detector	Gas alimentación	Volumen de inyección	Lecho	Temperatura análisis
TOC	Shimadzu TOC-V CSH con módulo para sólidos SSM-5000A	Cálculo conversión TOC de citrato	Infrarrojo no dispersivo (NDIR)	Aire de alta pureza 99.995 % 150 $mL \cdot min^{-1}$	100 µL	Tubo de combustión relleno con catalizador de Pt y lana de vidrio.	680 ºC

Técnica de análisis	Equipo	Finalidad	Acondicionamiento de muestras	Reactivo de análisis	Rango de detección
Colorimetría	Colorímetro DR/890 (Hach)	Cuantificación de hierro total en disolución	· Se prepara un blanco con agua Milli-Q, se añade el reactivo FerroVer®, se deja reaccionar durante 3 minutos y se establece el cero. · Se diluyen 150 µL de muestra en 10 mL de agua Milli-Q · Se añade el reactivo FerroVer y se deja reaccionar durante 3 minutos · Se lee el valor proporcionado por el equipo	FerroVer®, contiene una sal de ácido 1,10-fenantrolin-p-toluenosulfónico	0 – 3 $mg \cdot L^{-1}$ de Fe
		Cuantificación de Fe(II) en disolución	· Se prepara un blanco con agua Milli-Q, se añade el reactivo para Fe(II), se deja reaccionar durante 3 minutos y se establece el cero. · Se diluyen 400 µL de muestra en 25 mL de agua Milli-Q · Se añade el reactivo para Fe(II) y se deja reaccionar durante 3 minutos · Se lee el valor proporcionado por el equipo ·	1,10fenantrolina y bicarbonato de sodio	0 – 3 $mg \cdot L^{-1}$ de Fe(II)

Técnica de análisis	Equipo	Finalidad	Resumen del ensayo	Reactivo de análisis
Microtox®	Analizador Microtox M500	Estudio de toxicidad de las muestras acuosas	· Se reconstituye el reactivo liofilizado (bacteria *Vibrio fischeri*) con la disolución reconstituyente. · Se realizan diluciones sucesivas ½ (dilución posterior es 1/ 2 de la anterior) de muestra problema con la disolución salina. · Se mide la disminución de luminosidad en el equipo pasados 5 y 15 minutos tras poner en contacto las sucesivas diluciones de la muestra con el reactivo. .	Reactivo Microtox liofilizado. Disolución salina 2% NaCl Disolución reconstituyente

4.

RESULTADOS Y DISCUSIÓN INTEGRADORA

En este capítulo se muestran los resultados de mayor relevancia, así como el análisis y las ideas extraídas de las diferentes publicaciones sobre las que está basada esta tesis doctoral. Para facilitar la exposición, los resultados se encuentran clasificados en 3 bloques, correspondiendo cada uno de ellos con el tipo de contaminante tratado (etilbenceno, biodiesel B20, e hidrocarburos aromáticos policíclicos).

Durante el desarrollo del trabajo, todos los experimentos llevados a cabos se realizaron con el mismo tipo de suelo, clasificado como franco arcillo arenoso, perteneciendo a un horizonte B_T de un área localizada en el municipio de Arganda del Rey, dentro de la Comunidad Autónoma de Madrid. Las propiedades y características de mayor relevancia aparecen publicadas en un trabajo previo a los desarrollados en esta tesis, que a su vez pertenece al mismo grupo de investigación (Vicente et al., 2012). En el trabajo de Vicente et al,. 2012, se estudió la aplicación del reactivo Fenton modificado sobre un suelo contaminado con un herbicida (Diuron), en concentraciones similares a las que se podían encontrar en un caso de suelo afectado por contaminación difusa. En la presente tesis doctoral, la línea que se ha seguido fue la de estudiar casos similares a situaciones de contaminación localizada, en la que las concentraciones de los contaminantes en el suelo es superior y además éstos se pueden llegar a encontrar también en forma de fases no acuosas por su elevada hidrofobicidad.

Las publicaciones derivadas del trabajo de esta tesis son las siguientes:

- Eliminación de etilbenceno como contaminante representativo de gasolinas.
    - Artículo 1: "*Remediation of soil contaminated by NAPLs using modified Fenton reagent: application to gasoline type compounds.*". Journal of Chemical Technology and Biotechnology 2015; 90: 754-764. Pardo F, Rosas JM, Santos A, Romero A.
- Eliminación de FAME e hidrocarburos alifáticos como contaminantes de un combustibl del tipo biodiesel B20.
    - Artículo 2: *"Remediation of a biodiesel blend-contaminated soil by using a modified Fenton process*." Environmental Science and Pollution Research 2014; 21: 12198-12207. Pardo F, Rosas JM, Santos A, Romero A.
    - Artículo 3: *"Remediation of a Biodiesel Blend-Contaminated Soil with Activated Persulfate by Different Sources of Iron."*. Water Air and Soil Pollution. 2015. 226: 12. Pardo F, Rosas JM, Santos A, Romero A.

- Eliminación de Hidrocarburos Aromáticos Policíclicos.
    - Artículo 4: "*Optimization of the application of the Fenton chemistry for the remediation of a contaminated soil with polycyclic aromatic hydrocarbons."*. Journal of Chemical Technology & Biotechnology. 2016. 91:6, 1763 – 1772. Pardo F, Peluffo M, Santos A, Romero A.
    - Artículo 5: *"Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil.* Science of The Total Environment. 2016. 563–564, 649–656. Peluffo M, Pardo F, Santos A, Romero A.
    - Artículo 6: *"Fate of iron and polycyclic aromatic hydrocarbons during the remediation of a contaminated soil using iron-activated persulfate: a column study"*. Science of the Total Environment. 2016. 566-567:480-8. Pardo F., Santos A., Romero. A.

4.1 Eliminación de etilbenceno (Artículo 1)

De acuerdo a lo que se indicó anteriormente, la selección de etilbenceno como contaminante fue realizada en base a sus particulares características dentro del grupo BTEX. Es el componente de menor volatilidad y que con mayor facilidad puede interaccionar y quedar retenido en el suelo, además de ser uno de los componentes mayoritarios detectados cuando se dan fugas de gasolina en estaciones de servicio, tuberías de transporte, etc. Por otro lado, la selección del reactivo Fenton modificado con citrato de sodio se debió a su ya mostrada eficacia para la eliminación de Diuron en experimentos con el mismo tipo de suelo (Vicente et al., 2012). En este sentido, no fue necesario realizar un ajuste previo del pH del medio en los tratamientos.

El estudio de la eliminación de etilbenceno utilizando el reactivo Fenton queda recogido en la parte de resultados y discusión del primer artículo. En la Tabla 4.1 aparecen resumidos todos los tratamientos llevados a cabo y las correspondientes conversiones de contaminante que se alcanzaron para cada tratamiento.

Oxidación del agente quelante

Un factor crítico a tener en cuenta durante la aplicación del reactivo Fenton modificado por la adición de agentes quelantes es que, a pesar de que aporta

importantes ventajas como mantener el catalizador en disolución (Fe(III)) a pH cercano a la neutralidad, la adición de especies oxidantes al medio puede resultar en una degradación del agente quelante, (Huang et al., 2009; Meichtry et al., 2011; Sillanpaa et al., 2011). Por este motivo, se realizó un estudio previo de la degradación de agente quelante en el medio aplicando el reactivo Fenton modificado sobre el suelo sin contaminar.

Atendiendo a los resultados obtenidos, se observó que en las condiciones de trabajo seleccionadas (C_{CT0} = 50 mmol·L^{-1}; $C_{H_2O_20}$ = 1470 mmol·L^{-1}; $C_{Fe(III)0}$= 5 mmol·L^{-1}) se alcanzó una eliminación completa de citrato, expresada en términos de conversión (Ec. [4.1]), a los 4 días de reacción (96 horas). Además, se observó que el hierro presente en disolución fue disminuyendo a medida que el citrato se iba degradando, desde su concentración inicial (5 mmol·L^{-1}) hasta un valor cercano a 1.5 mmol·L^{-1}.

$$X_{CT} = \frac{C_{CT\,0} - C_{CT}}{C_{CT_0}} \qquad [4.1]$$

Por otra parte, de la degradación del citrato de sodio se observó que, a pesar de haberse degradado en un 98.2%, el grado de mineralización, expresado a partir de la concentración de carbono orgánico total (%) de las muestras (TOC), Ec. [4.2], fue de un 26%.

$$\%_{mineralización} = \frac{TOC_0 - TOC}{TOC_0} x100 \qquad [4.2]$$

<u>Efecto de la concentración de contaminante</u>

El estudio del efecto de la concentración de contaminante se realizó modificando la cantidad de etilbenceno (0, 9.4, 18.8, 62 y 188 mmol$_{EB}$·kg^{-1}, respectivamente) presente en el suelo, se mantuvieron fijas: la concentración inicial de oxidante ($C_{H_2O_20}$ = 1470 mmol·L^{-1}), la concentración inicial de catalizador ($C_{Fe(III)0}$ = 5 mmol·L^{-1}) y la concentración inicial de citrato de sodio (C_{CT0} = 50 mmol·L^{-1}). De los resultados se deduce que tras aumentar la concentración inicial de contaminante en el suelo, la conversión de oxidante disminuye. Además, como resultado de la competencia entre etilbenceno y citrato por el agente oxidante, la degradación del agente quelante fue cada vez más lenta conforme aumentaba la concentración inicial de contaminante. Por

último, las limitaciones al transporte de la fase orgánica (etilbenceno) a la fase acuosa, dado que la reacción de oxidación del contaminante tiene lugar en la fase acuosa, resultaron en una disminución notable en la conversión de contaminante cuando su concentración fue mayor, pasando de X_{EB} superiores al 95% cuando la concentración inicial de contaminante fue inferior a C_{EB0} = 188 $mmol_{EB}\cdot kg^{-1}$ a X_{EB}~50% cuando su concentración inicial en el suelo (C_{EB0}) fue de 188 $mmol_{EB}\cdot kg^{-1}$. En la Ec. [4.5], se muestra como la conversión de etilbenceno (X_{EB}) depende indirectamente de su concentración inicial en el suelo ($mmol\cdot kg^{-1}$).

$$X_{EB} = \frac{C_{EB_0} - C_{EB}}{C_{EB_0}} \qquad [4.3]$$

$$-\frac{dN_{EB}}{dt} = k \cdot C_{H2O2}^{n} \cdot C_{EB}^{*} \cdot V_L \qquad [4.4]$$

$$X_{EB} = \frac{N_{EB_0} - N_{EB}}{N_{EB_0}} = \frac{k \cdot C_{H2O2}^{n} \cdot C_{EB}^{*} \cdot t}{C_{EB_0}} \cdot \frac{V_L}{W_S} \qquad [4.5]$$

Efecto de la concentración de peróxido de hidrógeno

Para estudiar la influencia de la concentración de oxidante, se consideraron dos situaciones distintas, por un lado se evaluó la variación de la concentración de peróxido sobre el suelo sin contaminar, manteniendo fijas las concentraciones iniciales de catalizador y quelante ($C_{Fe(III)0}$=5 $mmol\cdot L^{-1}$ y C_{CT0}=50 $mmol\cdot L^{-1}$), y en el suelo contaminado con 188 $mmol_{EB}\cdot kg^{-1}$. No se observaron diferencias significativas en relación al suelo sin contaminar, pero en el suelo contaminado se pudo apreciar que, debido a que la transferencia entre fases controlaba la reacción, a mayor concentración de agente oxidante (menor relación molar H_2O_2/EB) en el suelo, la conversión de peróxido, citrato y el propio contaminante, fueron menores.

Efecto de la concentración de catalizador

El estudio de la influencia de la concentración de hierro en la reacción se realizó modificando su concentración inicial manteniendo fijas las siguientes condiciones iniciales: $C_{H_2O_20}$ = 1470 $mmol\cdot L^{-1}$, C_{CT0} = 50 $mmol\cdot L^{-1}$, C_{EB0} = 0.094 $mmol\cdot kg^{-1}$. Se observó que, a pesar de aumentar 5.4 veces la concentración de hierro en la disolución, de 5 a 27 $mmol\cdot L^{-1}$ las diferencias entre las distintas variables del proceso no fueron tan

destacadas. Por ejemplo, en caso del etilbenceno, la mayor diferencia que se apreció fue que con menos concentración de hierro inicial $C_{Fe(III)0}$ = 5 mmol·L^{-1} se alcanzó la conversión casi completa del contaminante más lentamente que cuando la dosis fue mayor ($C_{Fe(III)0}$ = 27 mmol·L^{-1}).

Efecto del suelo

Siendo el contacto entre fases un factor crucial para comprender los mecanismos de eliminación de etilbenceno, se realizaron dos tipos de experimentos con este propósito. Por un lado, se añadió una disolución con oxidante, catalizador y agente quelante sobre el contaminante, que se encontraba en forma de fase orgánica no acuosa, y por otro lado, se llevó a cabo la reacción, con las mismas concentraciones iniciales de oxidante, catalizador, agente quelante, sobre suelo contaminado con etilbenceno. Tras haber comprobado anteriormente que la transferencia entre fases limitaba la velocidad de reacción, se observó que, con el contaminante distribuido sobre las partículas de suelo, el contacto entre fases fue mejor que cuando la reacción se dio entre fases líquidas (acuosa y orgánica). Esta mejora en la transferencia entre fases se comprobó también en los respectivos perfiles de oxidante, contaminante, y agente quelante. Es preciso destacar que, a pesar de mejorar la transferencia entre fases, debido al mayor consumo improductivo de oxidante en el suelo, la conversión final de etilbenceno fue bastante similar en ambos casos (X_{EB}~60%).

Estudio de ecotoxicidad

Por último, se realizaron una serie de ensayos de ecotoxicidad sobre la fase acuosa procedente de las reacciones, antes y después de la aplicación del reactivo Fenton modificado. Estos ensayos, siguiendo el protocolo Microtox©, se realizaron a partir de la predicción de las unidades de toxicidad de las muestras analizadas (TU's), considerando el etilbenceno como la especie de mayor contribución a la toxicidad de la muestra, calculadas por la Ec. [4.6], donde C_{EB} es la concentración de etilbenceno en la fase acuosa y EC_{50} es la concentración de contaminante a la que la intensidad de luz que emiten las bacterias del ensayo se reduce a la mitad. De esta manera se consiguió estudiar, no sólo la eficiencia de la técnica en términos de eliminación de contaminante, sino también en relación a su potencial a la hora de reducir la toxicidad del medio una vez llevada a cabo la técnica. En estos ensayos de ecotoxicidad se observó que tras los

tratamientos, la toxicidad de las fases acuosas disminuyó, confirmando por tanto la ausencia de productos de oxidación de etilbenceno de mayor toxicidad.

$$TU's = \frac{C_{EB_{g\cdot L^{-1}}}}{EC50_{g\cdot L^{-1}}} \qquad [4.6]$$

Tabla. 4.1. Resumen de las eficiencias de eliminación para cada uno de los diferentes tratamientos llevados a cabo en la aplicación del reactivo Fenton modificado para la eliminación de etilbenceno. Tª = 20 ºC, sin ajuste previo del pH del medio. W_S = 5 g, V_L= 10 mL, C_{CT0} = 50 mmol·L^{-1}. Tiempo máximo de tratamiento: 6 días.

Peso suelo (g)	***Relación suelo/fase acuosa mL·g^{-1}***	***mmol EB***	***C_{EB0}***		***$C_{H_2O_20}$***		***$C_{Fe(III)0}$***		***X_{EB}^{final}***
			mmol·kg^{-1}	***mg·kg^{-1}***	***mmol·L^{-1}***	***mg·L^{-1}***	***mmol·L^{-1}***	***mg·L^{-1}***	
5	2	0.047	9.4	1000	1470	50000	5	280	98%
5	2	0.094	18.8	2000	1470	50000	5	280	95%
5	2	0.310	62.0	6600	1470	50000	5	280	97%
5	2	0.940	188	20000	1470	50000	5	280	49%
5	2	0.940	188	20000	4410	150000	5	280	60%
5	2	0.094	18.8	2000	1470	50000	27	1500	98%
0	0	0.094	-	-	1470	50000	27	1500	96%
0	0	0.940	-	-	4410	150000	5	280	59%

ARTÍCULO 1/ ARTICLE 1

Título/*Title*: Remediation of soil contaminated by NAPLs using modified Fenton reagent: application to gasoline type compounds.

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Estado actual/*current status*: Journal of Chemical Technology and Biotechnology. Abril / *April* 2015. 90:4, 754–764.
Recibido/*Received*: 15-01-2014. Revisado/*Revised*: 7-03-2014. Aceptado para publicación/*Accepted for publication*: 13-03-2014. Publicado Online/*First Published online*: 07-04-2014.

DOI: 10.1002/jctb.4373

Factor de impacto/Impact factor (JCR, 2014): 2.349

Research Article

SCI

Received: 15 January 2014 Revised: 7 March 2014 Accepted article published: 13 March 2014 Published online in Wiley Online Library:

(wileyonlinelibrary.com) DOI 10.1002/jctb.4373

Remediation of soil contaminated by NAPLs using modified Fenton reagent: application to gasoline type compounds

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Abstract

BACKGROUND: A modified Fenton reaction was used for the remediation of a soil polluted with ethylbenzene (EB), a toxic compound in gasoline. Fe(III) and trisodium citrate were used as catalyst and chelating agent, respectively. pH remained near-neutral during the process. Contaminant, chelating agent, oxidant and iron in solution were monitored at all times. A comparison between slurry (aqueous-organic and soil phases) and liquid systems (aqueous-organic phases) was carried out.

RESULTS: EB conversion increased as H_2O_2/EB ratios rose, for a given EB concentration. Furthermore, the contaminant conversion was decreased as the EB concentration increased, at a fixed H_2O_2/EB ratio. This indicates that the reaction takes place in the aqueous phase, with the oxidation rate limited by the EB concentration in this phase. The presence of soil produces a better contact between phases, enhancing EB transport from the organic to the aqueous phase. As EB was oxidized in the aqueous phase, the toxicity of this phase decreased, because non-toxic oxidation byproducts were obtained. The chelant was oxidized, but not totally mineralized. This chelant oxidation produces precipitation of the catalyst from the aqueous phase.

CONCLUSIONS: The results suggest the suitability of modified Fenton reaction to remediate contaminated soils with non-aqueous phase liquids.

Keywords: ethylbenzene; gasoline; NAPLs; modified-Fenton; soil remediation; ecotoxicity

INTRODUCTION

Contamination of soils and groundwater by the presence of diesel or gasoline can result in serious environmental and health problems if identification of the contaminant source, and management and treatment of the pollutants are not undertaken adequately and quickly.[1] Diesel and gasoline are a clear example of local contamination sources due to accidental spills and leaks from underground storage tanks or pipelines. These compounds are usually found in soil as nonaqueous phase liquids (NAPLs). These NAPLs can be chemically or physically attached to soil particles, and the majority of the pollutant is trapped in small spaces between soil particles[2] and can migrate through the soil to the water table, leading to the dual problem of soil and groundwater contamination.[3]

For the remediation of NAPL contaminated soils, *in situ* chemical oxidation (ISCO) is an effective technique, already implemented, which is based on the injection of a strong oxidant into the contaminated soil to degrade the pollutants.[4] Among the ISCO techniques, Fenton reaction has been studied for the remediation of soils contaminated with different types of NAPLs: light nonaqueous phase liquids (LNAPLs) which have densities less than that of water, such as diesel[4–6] and BTEX;[7,8] and dense nonaqueous phase liquids (DNAPLs) which have densities greater than that of water, such as PAH[9] or chlorinated compounds.[10] Fenton reaction consists of the combination of H_2O_2 with a soluble catalyst (Fe(II) or Fe(III)), and as a result of this interaction, a strong oxidant such as hydroxyl radicals ($E° = 2.73$ V) are released, having the ability to oxidize a wide range of organic compounds.

In spite of this, the application of Fenton reaction to contaminated soils has some drawbacks that have to be taken into account: hydroxyl radicals are short lived;[9] there could be excessive consumption of the oxidant due to nonproductive reactions between H_2O_2 and soil compounds associated with the instability of hydrogen peroxide with water and oxygen, when it contacts inorganic compounds, such as iron and manganese oxyhydroxide catalysts, as well as other transition metals resulting from mineral dissolution, or with organic compounds, which are widespread in surface soils;[11,12] and finally, the addition of chelating compounds is necessary to avoid the loss of catalyst, due to precipitation of iron in the form of $Fe(OH)_3$ at the near-neutral pH usually found in most soils.[13,14] Because of this, the use of nontoxic and biodegradable chelating agents has been proposed as a useful tool to overcome this disadvantage.[9,11,14–16] Citrate complies with these requirements as chelating compound, and its addition, as sodium salt instead of the acidic form, promotes a near-neutral soil pH during reaction, minimizing the environmental impact of the remediation technique. This sodium citrate is also able to keep iron in solution

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due to its ability to bind ferrous and ferric iron, and can also minimize the nonproductive consumption of hydrogen peroxide.[11,17]

Modified Fenton reactions (MFR) produce lower contaminant removal in short times, but over time, contaminant elimination significantly increases due to the ability of the chelating agent to keep the catalyst in solution for longer periods of time.[18] Although chelating agents can compete with pollutants for hydroxyl radicals,[19] the oxidation of chelating agents by advanced oxidation processes (AOPs) has been studied only in the aqueous phase. As examples, Meichstry *et al.*[20] proposed a reaction mechanism through the analysis of citrate oxidation intermediates by carrying out a photocatalytic reaction with TiO_2; Huang *et al.*[21] studied citrate degradation by photo-Fenton and electro-Fenton processes; and Sillanpaa *et al.*[22] made a comparison of the oxidation of some chelating agents such as EDTA, NTA, DTPA and HEDTA by several AOPs, such as ozonation, Fenton or Fenton-like. In contrast, the monitoring of chelating agents when using the Fenton process for soil remediation is an issue that has been scarcely considered in the literature.[23] However, the evolution of the chelating agent, and its relationship with the catalyst (Fe(III)) in the MFR is a critical factor that must be evaluated for the implementation of remediation by ISCO.

The aim of this present work is to analyze the effect of both catalyst and oxidant concentrations on the oxidant consumption, chelating agent oxidation, contaminant conversion and Fe(III) remaining in solution in a contaminated soil. For this study, ethylbenzene (EB) was selected as a representative NAPL. EB is one of the most toxic compounds in gasoline, being listed as one of the US EPA priority pollutants,[24] and, as a BTEX component (Benzene, Toluene, Ethylbenzene and Xylene), its removal from gasoline fractions results in a decrease of gasoline toxicity.[25,26] Moreover, among BTEX, EB is the least volatile (900 Pa of vapor pressure at 20 °C) and most persistent for degradation in soils.[25] Trisodium citrate was chosen as chelating agent due to its biodegradability, nontoxic nature, and for its proved efficiency in enhancing Fenton reaction. A comparison of the results obtained with soil (slurry reaction) and without soil (aqueous-organic media) was also carried out.

EXPERIMENTAL

A sandy clay loam B_T horizon from the Autonomous Community of Madrid with neutral pH was selected for this work. Soil characterization procedures are described elsewhere.[23] The most important soil properties are listed in Table 1.

Table 1. Properties of the soil used for remediation experiments (standard deviation 4–7%)

Soil organic mater (SOM) %		0.365
Total organic carbon (TOC) /%		0.196
SOM fractions/%	Labile Pool I	0.114
	Labile Pool II	0.012
	Recacitrant	0.07
Total carbon (TC) %		0.198
Inorganic carbon (IC) %		0.002
pH		7.22
Apparent surface area (Sg^{BET}) $m^2\ g^{-1}$		23
Pore volume $cm^3\ g^{-1}$		0.031
[Mn] $mg\ g^{-1}$		0.170
[Fe] $mg\ g^{-1}$	Total	18.2
	amorphous	0.525
	crystalline	6.710

Reagents

Reagents of analytical grade were used in the experiments. Ethylbenzene 99% and trisodium citrate 2-hydrate (CT) ≥99.0% were purchased from Sigma–Aldrich. H_2O_2 > 30% (w/w) was provided from Fisher Chemical. Sulfuric acid >95%, from Fisher Chemical, and potassium permanganate 99.5%, from Panreac, were both used in the determination of H_2O_2. Ferric sulfate, from Panreac, was used as the catalytic Fe(III) specie. Sodium carbonate 99.8% and sodium bicarbonate 99.7%, both purchased from Panreac, were used as mobile phase compounds for the ionic chromatography. Methanol of supragradient HPLC grade, from Fisher Chemical, was used as solvent, extracting agent for soil samples and quenching agent for the oxidation reactions. Acetonitrile HPLC gradient grade, used as mobile phase in HPLC for EB analysis, was obtained from Fisher Chemical. Nitric acid 69.5%, obtained from Scharlau, was utilized as stabilizer of iron ions in MP-AES analysis. Both phosphoric acid ≥85% and potassium phosphate monobasic ≥99.5%, purchased from Sigma-Aldrich, were used as mobile phase in HPLC for the analysis of citrate oxidation products. Oxalic acid dihydrate (99.5%, Merck), Malonic acid (99%, Merck) and 3-Oxoglutaric acid (Technical grade, Aldrich) were used to make standard solutions for their possible identification in citrate oxidation reaction. Ultrapure laboratory grade water (MilliQ) obtained from a deionizing system was used for the preparation of all solutions.

Set-up and procedure

All experiments were performed in batch mode, without adjustment of pH. 50 mL PTFE centrifuge tubes closed with a PTFE screw top cap were used as reactors, which were stirred isothermally (20 °C) by orbital shaking (SW22 equipment supplied by Julabo) at 200 rpm. A concentration of 50 mmol L^{-1} of CT was selected.[11,17] Each reaction tube represents one time point. Replicate tubes were sacrificed and analyzed at specified time periods of 24, 48, 72, 96 and 120 h. Duplicate tests were performed for each experiment, with differences lower than 10%. The corresponding average values are reported. A third tube was sacrificed at 72 h to measure pH in the reaction. For comparison, reactions were carried out with and without soil. Both procedures are described below. All the experiments carried out are summarized in Table 2.

Slurry reactions (soil-organic-aqueous phases)

Contaminated soil was artificially prepared using uncontaminated control soil. The soil was spiked by adding different amounts of EB to 5 g of clean soil. The initial concentrations used were in the range 188 to 9.4 $mmol_{EB}\ kg_{soil}^{-1}$. Spiked soils were stirred to achieve complete homogeneity.

In each experiment 10 mL of aqueous phase containing the oxidant (hydrogen peroxide), chelating agent (CT) and catalyst (ferric sulfate) was added to 5 g of contaminated soil, in 50 mL PTFE centrifuge tubes. The aqueous phase liquid volume to soil mass ratio (V_L/W) used was 2 mL g^{-1}.

At the reaction times specified below, 15 mL of methanol was added to the slurry to blend the supernatant, quench the reaction and extract the contaminant from the soil. Ultrasonic solvent extraction was the selected method. Reaction samples were sonicated for 1 h with the solvent mixture in an ultrasonic bath (Powersonic 505) at room temperature, followed by centrifugation for

Table 2. Experimental conditions for runs carried out in batch tests: T = 20 °C , $C_{Citrate}$ = 50 mmol L^{-1}

Run	W soil g	Total EBmmol	H_2O_2 Mmol L^{-1}	Fe(III) concentration mmol L^{-1}	H_2O_2/EB molar ratio	V_L mL
1	5	0	1470	5	-	10
2	5	0.047	1470	5	313	
3	5	0.094	1470	5	156	
4	5	0.310	1470	5	47	
5	5	0.940	1470	5	16	
6	5	0.940	4410	5	47	
7	5	0	4410	5	-	
8	5	0.094	1470	27	156	
9	0	0.094	1470	27	156	
10	0	0.940	4410	5	47	

10 min with a Meditronic-BL (Selecta) centrifuge. No consumption of hydrogen peroxide was detected during sonication. The resulting supernatant was used to determine CT, EB, iron and hydrogen peroxide concentrations. It was checked that all the EB in the slurry was transferred to the supernatant during this extraction.

For determination of the total organic carbon (TOC) and ecotoxicity of the aqueous phase after remediation, a reaction tube corresponding to the final time (120 h) was directly centrifuged without previous addition of methanol; the supernatant was separated and decanted, in order to avoid the presence of organic droplets of NAPLs.

Aqueous-organic phase reactions

Aqueous samples were contaminated by adding different amounts of EB to 10 mL of water containing the chelating agent and catalyst (ferric sulfate). Afterwards, oxidant was added (that corresponds to zero time). Experimental conditions related to the aqueous-organic phase reactions are summarized in Table 2 (runs 9–10).

At the desired times, 15 mL methanol was added to the reaction tubes and these were cooled down for 8 h at −18 °C, in order to blend organic and aqueous into one liquid phase and to quench the oxidation reaction.[26] From this liquid blended phase, trisodium citrate, iron, hydrogen peroxide and EB were determined as indicated in their respective analytical methods.

Ecotoxicity of an aqueous sample obtained after centrifugation of a mixture of 0.940 mmol EB in 10 mL of water (containing 50 mmol L^{-1} of citrate and 5 mmol L^{-1} of iron III) was also measured as a blank test.

Analytical method

Determination of EB and citrate concentrations, and the detection of aromatic intermediates and citrate oxidation products were carried out by HPLC (Agilent, model 1100). 5 μL of sample were injected into a high-performance liquid chromatography column, Chromolith RP-18e 100–4.6 mm, with an Agilent 1290 Infinity Diode Array Detector.

For EB and aromatic oxidation intermediates analysis, the mobile phase selected was acetonitrile–water (70:30, v/v) with a flow rate of 0.2 mL min^{-1}. The effluent was monitored at 208 nm, the maximum absorbance wavelength of EB. The programmed temperature of the column during analysis was 40 °C. Reaction samples were prepared by adding 0.9 mL of methanol to 0.1 mL of quenched reaction sample. The corresponding detection limit was 1.1 mg L^{-1} EB.

For citrate oxidation products analysis and citrate quantification, a buffer solution with 20 mmol L^{-1} $H_2P_2O_4$, acidified to pH = 2.1 with phosphoric acid, was used, and a flow rate of 0.2 mL min^{-1}. The programmed temperature of the column during analysis was 20 °C. Reaction samples were prepared by adding 0.9 mL of buffer phosphate mobile phase to 0.1 mL of quenched reaction sample, the corresponding detection limit was 6.1 mg L^{-1} CT.

Ionic chromatography was used to complement the identification of organic acids carried out with HPLC. A 761 compact ionic chromatograph was employed, selecting a Metrosep A supp10 column, for anion analysis, with chemical suppression. A mobile phase composed of Na_2CO_3 and $NaHCO_3$, both with 5 mmol L^{-1} concentration, and a flow rate of 1 mL min^{-1} were used.

Prior to H_2O_2 determination, it was confirmed that methanol did not interfere with its analysis. The concentration of H_2O_2 in solution was determined by titration with a solution of potassium permanganate, $KMnO_4$, of known concentration, in sulfuric acid by using a potentiometric titration analyzer supplied by Metrohm. pH was measured with a pH glass electrode also supplied by Metrohm.

Analysis of iron was carried out with a microwave plasma-atomic emission spectrometer 4100 MP-AES (Agilent Technologies), an OneNeb nebulizer was used. A sample previously acidified with 1% (v:v) HNO_3 was fed into the MP-AES with a peristaltic pump operating at 8 rpm. The selected wavelength for iron determination was 259.94 nm.

The TOC content for liquid and solid samples (standard procedure EN 13137) was measured using a Shimadzu TOC-V CSH analyzer with a SSM-5000A solid sample module. Liquid samples were previously acidified in order to remove inorganic carbon (CO_2 dissolved). The toxicity of the aqueous supernatant was determined by the standard Microtox test procedure (ISO 11348–3, 1998) using a Microtox M500 analyzer (Azur Environmental). This standard test is based on the decrease of light emission by photobacterium phosphoreum resulting from the exposure to a toxicant. The microorganisms were Microtox Acute Reagent (Vibrio Fischeri) supplied by I.O. Analytical. Although the Microtox test gives the response of only one type of organism (Vibrio Fischeri bacterium) to the toxic exposure, the Microtox test is a very rapid, cost-effective, and widely accepted method for toxicity determination used extensively in the literature focusing on environmental issues.[27]

RESULTS AND DISCUSSION

First, the citrate conversion, including also the possible oxidation products and mineralization, was analyzed during MFR using

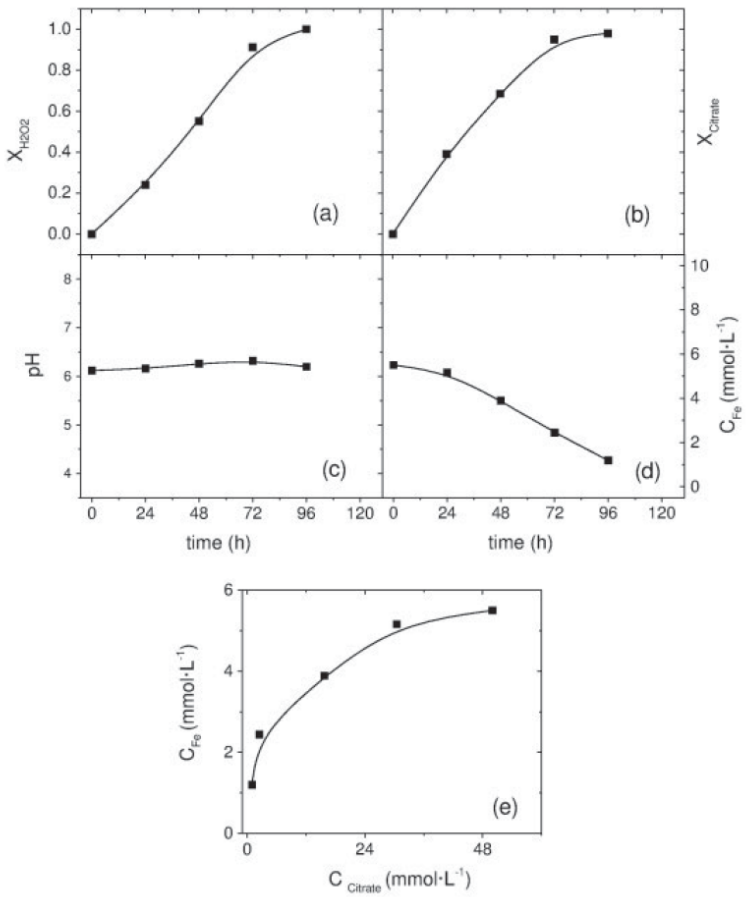

Figure 1. Evolution of the reaction media in the absence of EB (run 1): (a) X_{H2O2} vs t; (b) $X_{Citrate}$ vs t; (c) pH vs t; (d) C_{Fe} vs t; and (e) C_{Fe} vs $C_{Citrate}$ at 20°C, $V_L/W_{soil} = 2$ mL g^{-1}, $C_{Citrate} = 50$ mmol L^{-1}, $C_{H2O2} = 1470$ mmol L^{-1}, $C_{Fe(III)} = 5$ mmol L^{-1}.

non-contaminated soil. Then, the effect of EB, oxidant and catalyst concentrations on the conversions of H_2O_2, citrate and EB, were evaluated. The evolution of the aqueous Fe concentration and its relationship with the remaining citrate was also studied. Besides, a comparison of the results obtained in slurry system (soil, organic and aqueous phases) and liquid system (aqueous-organic phases) using the same EB, oxidant and catalyst dosages was also accomplished, with the goal of evaluating the effect of soil on the oxidant, chelating agent, and pollutant conversions.

Finally, the results obtained using an ecotoxicity bioassay (Microtox) are presented to discuss the effectiveness of Fenton reagent in terms of toxicity changes in the aqueous phase.

Citrate oxidation by MFR

First of all, it is important to mention that the amount of Fe extracted with 50 mmol L^{-1} of CT, when equilibrium was reached, was 0.3 mmol L^{-1}.[17] This value was quite low and the addition of catalyst from an external source became necessary to perform the MFR.

A run (run 1) consisting of the addition of 50 mmol L^{-1} CT, 5 mmol L^{-1} Fe(III) and 1470 mmol L^{-1} H_2O_2 over an uncontaminated soil was performed in order to evaluate the possible removal of citrate by adding H_2O_2 and Fe(III), and its possible oxidation products. Figure 1(a) and (b) show the H_2O_2 and citrate conversions as a function of the reaction time, respectively. Meanwhile, Fig. 1(c) and (d) represent the pH and aqueous iron concentration as a function of the reaction time, respectively. Figure 1(e) depicts the remaining iron concentration as a function of the aqueous citrate concentration.

As can be seen, the profiles of citrate and H_2O_2 conversions with time show similar trends. Almost total conversions of both species are reached near 72 h reaction. The presence of citrate as sodium salt controls the H_2O_2 conversion and keeps a neutral pH.[11] Taking into account that pH remains neutral during the reaction, the amount of soluble iron decays as citrate (chelating agent) disappears from the reaction media, as can be seen in Fig. 1(e). If citrate is not added, the iron in solution, at neutral pH, is negligible (<0.1 mmol L^{-1}).

At a reaction time of 96 h, citrate conversion was almost complete, but mineralization was only about 26%, due to the formation of different oxidation products. The main reaction products identified during the citrate oxidation by hydroxyl radicals were malonic acid (1700 mg L^{-1}), 3-oxoglutaric acid (350 mg L^{-1}) and oxalic acid (10 mg L^{-1}), in agreement with data previously reported in

Table 3. Carbon balance for citrate oxidation in run 1

	mg compound L^{-1}		mg carbon L^{-1}	
Compound	t = 0	t_f = 96 h	t = 0	t_f = 96 h
TOC measured			3600	2664
TOC removed (as CO_2)				936
Citrate	9450	174	3600	11
Malonic acid	0	1700	0	588
3-Oxoglutaric acid	0	355	0	146
Oxalic acid	0	10	0	1.3
TOC in identified compounds				746
TOC in non- identified compounds				1918

the literature.[20] These results are summarized in Table 3. As can be observed, 73% of the total organic carbon measured in the aqueous phase after citrate oxidation corresponds to non-identified compounds Adsorption of citrate in the absence of iron, oxidant and pollutant was also tested, and was negligible compared with the amount of citrate in solution, in agreement with previous results.[11,17]

Effect of EB concentration

The influence of EB concentration on the evolution of all species in the slurry system was analyzed using soils with different concentrations of EB, at the same dosages of hydrogen peroxide, ferric iron and trisodium citrate (Table 2: runs 1 to 5). The time evolution of the oxidant, chelating agent, contaminant, and iron in solution is shown in Fig. 2(a)–(d), respectively. The relationship between the remaining iron and chelating agent in solution is shown in Fig. 2(e). The pH values measured at 72 h are included in the legend of the figure.

As is shown in Fig. 2(a), as initial EB concentration decreases the oxidant conversion increases. However, under the experimental condition used here, the hydrogen peroxide conversion is not increased when oxidant to EB ratios above 313 mol_{H2O2} mol_{EB}^{-1} are used. In the same way, citrate oxidation is faster in the absence of

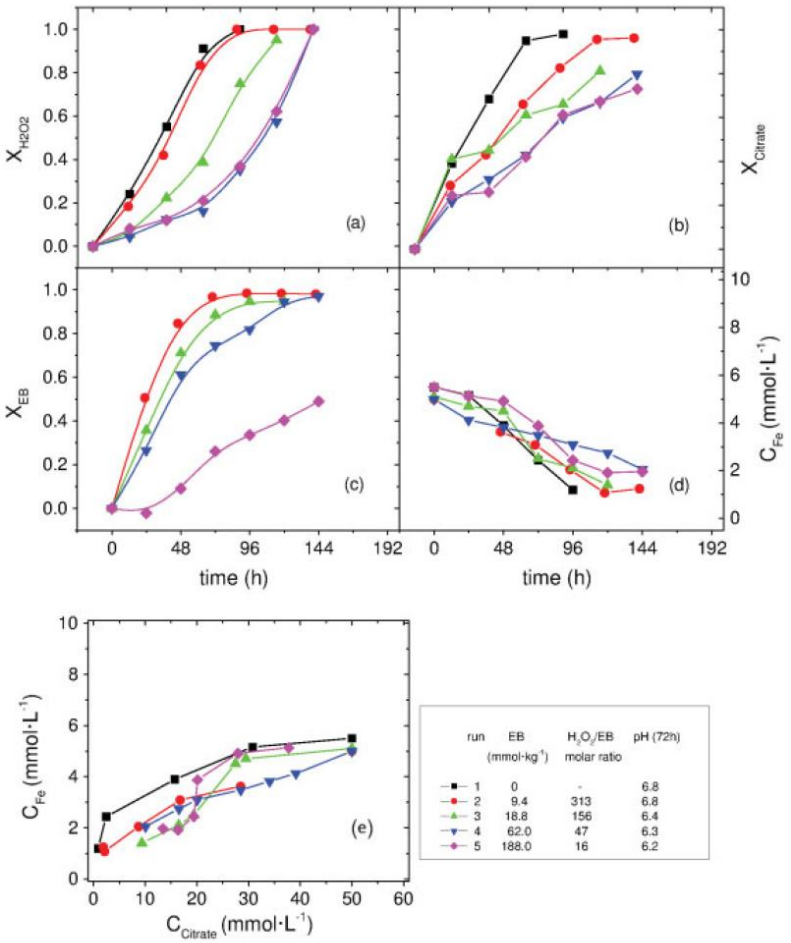

Figure 2. Influence of ethylbenzene concentration in soil on the evolution of reaction media: (a) X_{H2O2} vs t; (b) $X_{Citrate}$ vs t; (c) C_{EB} vs t; (d) C_{Fe} vs t; and (e) C_{Fe} vs $C_{Citrate}$ at 20°C, V_L/W_{soil} = 2 mL g^{-1}, $C_{Citrate}$ = 50 mmol L^{-1}, $C_{Fe(III)}$ = 5 mmol L^{-1} C_{H2O2} = 1470 mmol L^{-1}.

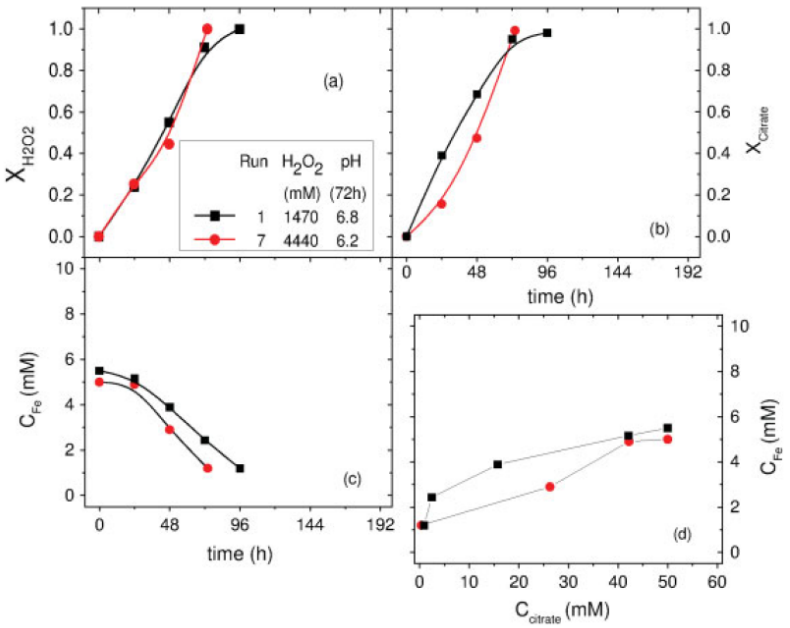

Figure 3. Influence of H_2O_2 concentration in soil on the evolution of the reaction media: (a) X_{H2O2} vs t; (b) $X_{Citrate}$ vs t; (c) C_{Fe} vs t; and (d) C_{Fe} vs $C_{Citrate}$, at 20°C, $V_L/W_{soil} = 2$ mL g^{-1}, $C_{Citrate} = 50$ mmol L^{-1}, $C_{Fe(III)} = 5$ mmol L^{-1}, $C_{EB} = 0$ mmol kg^{-1}.

EB (Fig. 2(b)). When EB is present in the reaction, the contaminant seems to compete with citrate for the hydroxyl radicals and, as a consequence, citrate conversion is slowed down.

It is observed in Fig. 2(c) that the increase of EB concentration (at a constant H_2O_2 concentration) produces a notable decrease in the EB conversion vs. time profile. This can be explained taking into account the low solubility of EB in the aqueous phase. If reaction takes place in the aqueous phase, the disappearance of EB in a batch system could be written (in the absence of mass transport resistances) as follows:

$$-\frac{dN_{EB}}{dt} = kC_{H2O2}^{n} C_{EB}^{*} V_L \quad (1)$$

with N_{EB} the mmol of EB in the slurry system, C_{EB}^{*} the solubility of EB in the aqueous phase (which is the maximum EB concentration than can be obtained in aqueous phase), V_L the volume of the aqueous phase, and k the kinetic constant. For a given time interval at which kC_{H2O2}^{n} can be assumed constant, the EB conversion could be calculated as:

$$X_{EB} = \frac{N_{EBo} - N_{EB}}{N_{EBo}} = \frac{kC_{H2O2}^{n} C_{EB}^{*}\, t\, V_{AP}}{N_{EBo}} = \frac{kC_{H2O2}^{n} C_{EB}^{*} t}{C_{EBo}} \frac{V_L}{W_{soil}} \quad (2)$$

at a given time, t, the numerator of Equation 2 yields a constant value, independently of the initial EB concentration in soil (C_{EBo} as mmol kg_{soil}^{-1}), but the denominator increases as C_{EBo} does. Therefore, a lower conversion is expected as C_{EBo} increases. If mass transport resistances are significant, the EB concentration in the aqueous phase, C_{EB}^{aq}, would be lower than the solubility, C_{EB}^{*}.

As was expected, iron in solution decreases as citrate concentration decays in the reaction media, as can be seen in Fig. 2(e).

In the case of an aged contaminated soil, the expected contaminant removal must be lower than that achieved for this artificially contaminated soil, due to lower contaminant availability[28,29] and an increase of the necessary oxidant dosage caused by unproductive reactions. However, the soil used has a very low SOM content, therefore, a high unproductive oxidant consumption is not expected due to these SOM compounds.

Effect of H_2O_2 concentration

The influence of hydrogen peroxide dosage on the MFR was studied over a non-polluted soil (runs 1 and 7) and over a soil contaminated with 188 mmol kg^{-1} of EB (runs 5 and 6). Figure 3(a)–(c) shows profiles of the oxidant, chelating agent, and iron in solution, over time, respectively. The evolution of the remaining iron as a function of the chelating agent concentration when the reaction takes place over uncontaminated soil is shown in Fig. 3(d). As can be seen in Fig. 3(a)–(b), the conversion vs time profiles are quite similar for the oxidant and chelant, at the H_2O_2/Fe(III) molar ratios used (294:1 in run 1 and 882:1 in run 7). Furthermore, complete consumption of the hydrogen peroxide, as well as total citrate oxidation, were reached at 72 h. Neutral/slightly acid pH was found in both these runs at 72 h (pH = 6.8 in run 1 and pH = 6.2 in run 7). Therefore, a change in hydrogen peroxide concentration in the range here tested does not seem to have a significant influence on the Fenton reaction, in the absence of EB in the media.

The effect of hydrogen peroxide concentration on the contaminated soil is collected in Fig. 4. In this case, a change of oxidant concentration has a significant effect on the oxidant, EB and chelating agent conversions, as can be observed in Fig. 4(a)–(c). Citrate oxidation and H_2O_2 consumption are enhanced when H_2O_2/EB molar ratio is increased. Total oxidant consumption was noted at both H_2O_2/EB molar ratios used. Citrate conversion was almost total at the highest value (H_2O_2/EB molar ratio 47:1). However, EB conversion was lower than unity in both cases because the oxidant was consumed. At the highest oxidant concentration used in runs 5 and

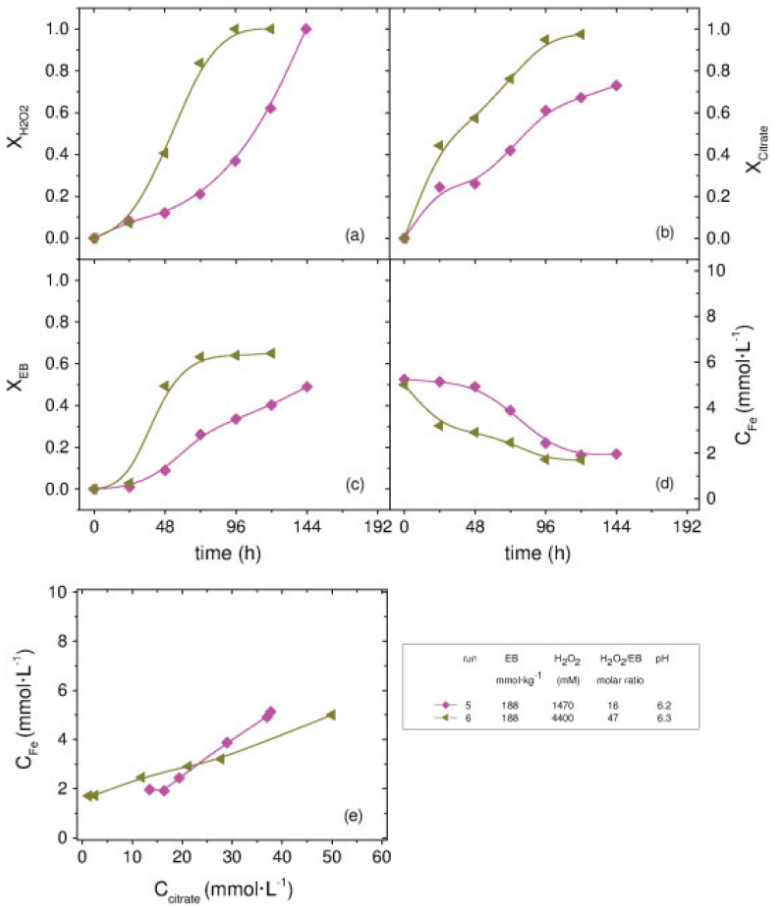

Figure 4. Influence of H_2O_2 concentration in soil on the evolution of the reaction media: (a) X_{H2O2} vs t; (b) $X_{Citrate}$ vs t; (c) C_{EB} vs t; (d) C_{Fe} vs t; and (e) C_{Fe} vs $C_{Citrate}$ at 20°C, $V_L/W_{soil} = 2$ mL g^{-1}, $C_{Citrate} = 50$ mmol L^{-1}, $C_{Fe(III)} = 5$ mmol L^{-1}, $C_{EB} = 188$ mmol kg^{-1}.

6, an EB final conversion of 60% was achieved, while 50% conversion was obtained at the lowest oxidant concentration.

By comparison of EB conversion in run 4 (Fig. 2(c) and run 6 (Fig.4(c)), it can be noticed that at the same H_2O_2/EB molar ratio, lower EB conversion is obtained at the highest EB concentration. This can be related, as mentioned before, to the low solubility of EB in aqueous phase (180 mg L^{-1} of pure component in distillated water at 20 °C[30]). Therefore, if the oxidation reaction takes place in the aqueous phase, the EB concentration in this phase limits the reaction extension and as a consequence, controls the oxidation process. This fact has not been systematically reported in the literature but it is in agreement with the higher efficiency noticed for NAPL compounds remediation, when these compounds are totally solubilized in the aqueous phase.[31]

As expected, the concentration of iron in solution decreases as citrate in the media diminishes, as can be seen in Figs. 4(d)–(e).

Effect of catalyst concentration

The influence of catalyst concentration on the evolution of the system was studied in a soil contaminated with 18.8 mmol kg^{-1} of EB, and by using concentrations of the oxidant, and citrate of 1470 and 50 mmol L^{-1}, respectively. The catalyst concentrations used were 5 mmol L^{-1} and 27 mmol L^{-1}, corresponding to runs 8 and 3, respectively.

Figure 5 shows the evolution of the different compounds involved in the reaction at the different catalyst concentrations. Oxidant and EB were consumed slightly faster when the concentration of Fe(III) was higher (27 mmol L^{-1}), as can be seen in Fig. 5(a) and (c), respectively. In spite of this slight improvement, total EB conversion is almost reached in both runs because the oxidant is totally consumed. On the other hand, similar citrate profiles with time are obtained at both catalyst concentrations used (Fig. 5(b)). The relationship between citrate and iron (Fig. 5(e)) indicates the remaining presence of iron in solution, once the reaction finished, at the highest Fe(III) concentration used.

Effect of soil

Results obtained using the same initial oxidant, pollutant, chelating agent and catalyst concentrations in slurry (soil-aqueous-organic phases) and liquid (aqueous-organic phases) systems have been compared. Data obtained in runs 6 and 10 are shown in Fig. 6. The corresponding results obtained in runs 8 and 9 are shown in Fig. 7.

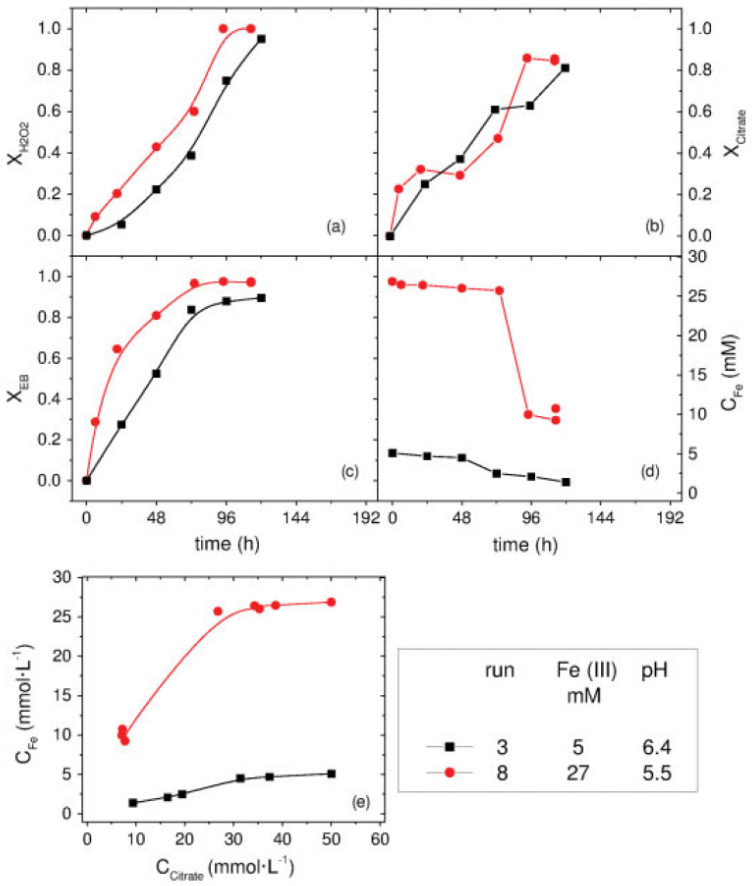

Figure 5. Influence of catalyst concentration in soil on the evolution of the reaction media: (a) X_2O_2 vs t; (b) $X_{Citrate}$ vs t; (c) C_{EB} vs t; (d) C_{Fe} vs t; and (e) C_{Fe} vs $C_{Citrate}$ at 20°C, $V_L/W_{soil} = 2$ mL g^{-1}, $C_{Citrate} = 50$ mmol L^{-1}, $C_{EB} = 94$ mmol kg^{-1}.

As can be seen in Figs 6(c) and 7(c), EB oxidation is faster in the slurry media than in the liquid one. This could be due to better transport of EB from the organic to the aqueous phase because of better interfacial contact among the different phases in the slurry media. A faster consumption of hydrogen peroxide and citrate are found in the slurry system, as shown in Figs 6(a)–(b) and 7(a)–(b).

As aforementioned, the amount of Fe(III) in solution can be related to the remaining amount of citrate because of the neutral pH obtained in both the slurry and aqueous systems, as can be observed in Figs 6(d)–(e) and 7(d)–(e). However, higher quantities of Fe(III) could be precipitated in the slurry media because of the presence of soil (Figs 6(d) and 7(d)).

The increase of the H_2O_2/EB molar ratio in runs 8 and 9 does not produce any significant change in the tendencies observed in runs 6 and 10, as can be deduced from the results reported in Figs 6 and 7. However, when higher H_2O_2/EB ratios and lower EB concentrations are used (see Fig. 7), higher EB conversions are obtained.

On the other hand, it is important to mention that real applications must take into account the possible biodegradation of EB and citrate, in addition to the removal by MFR.[32] Although they were negligible in the range of times evaluated in this work.

Ecotoxicity of the aqueous phase after remediation

EB concentration in the aqueous phase and ecotoxicity of this aqueous phase were measured in run 3, at 120 h, obtaining values of 0.47 mmol L^{-1} and 7.47 toxicity units (TUs), respectively. It should be noticed that hydrogen peroxide has been consumed at this reaction time.

For comparison, a blank sample obtained after centrifugation of a mixture of 0.094 mmol of EB and 10 mL of an aqueous solution (with 50 mmol L^{-1} of citrate and 5 mmol L^{-1} of Fe(III) was also used. EB in the aqueous phase was measured as 1.4 mmol L^{-1} and a value of 19.7 TUs was obtained for this aqueous phase.

The effective concentration value (EC_{50}) of EB by Microtox bioassay given in the literature was 0.0907 mmol L^{-1}.[33] If the only toxic compound in the aqueous phase were EB, TUs of an aqueous phase, containing a known concentration of this compound, could be predicted by means of Equation 3.

$$TU's = \frac{[EB]_{mg\cdot L^{-1}}}{EC_{50} mg\cdot L^{-1}} \quad (3)$$

In this way, TUs predicted for the aqueous phase in run 3 after 120 min are 5.18 while TUs predicted for the aqueous phase of the blank run are 15.6. Both values are close to the experimental ones.

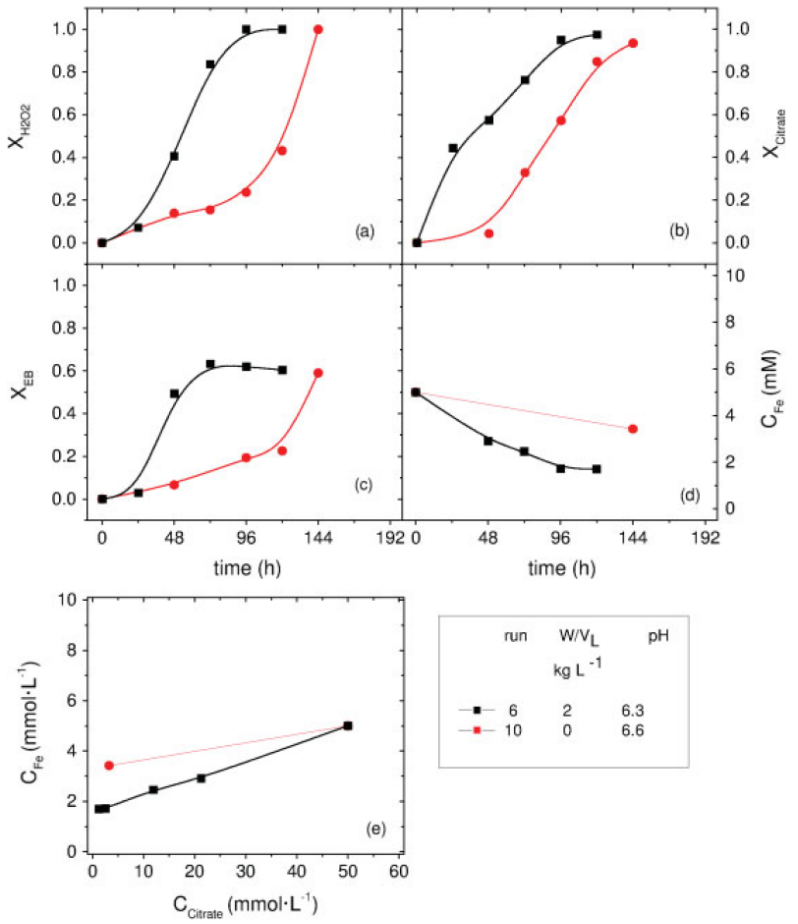

Figure 6. Influence of the presence of soil on the evolution of the reaction media: (a) X_{H2O2} vs t; (b) $X_{Citrate}$ vs t; (c) C_{EB} vs t; (d) C_{Fe} vs t; and (e) C_{Fe} vs $C_{Citrate}$ at 20°C, $V_L/W_{soil} = 2$ mL g^{-1}, $C_{Citrate} = 50$ mmol L^{-1}, $C_{Fe(III)} = 5$ mmol L^{-1}, $C_{EB} = 188$ mmol kg^{-1}, $C_{H2O2} = 4400$ mmol L^{-1}.

Consequently, it can be assumed that non-toxic compounds are released to the aqueous phase during EB oxidation. This fact is also supported by the absence of aromatic intermediates confirmed by HPLC analysis, which is a remarkably finding for ISCO implementation.

CONCLUSIONS

MFR has been used for the remediation of a soil contaminated with ethylbenzene (EB) as NAPL at neutral pH. EB was selected among all BTEX due to its high toxicity and persistence in soil to remediation techniques.

The identification of the oxidation products of citrate oxidation was done with uncontaminated soil in a slurry system. After complete citrate oxidation, only 26% mineralization was obtained under the experimental conditions tested, due to the formation of organic byproducts, such as oxalic, malonic and 3-oxoglutaric acid. As long as citrate is oxidized, Fe(III) in solution decreases, therefore, it is desirable to keep citrate in solution for as long as possible, to improve the effectiveness of the modified Fenton reaction. In spite of the competition between chelant and EB for the oxidant, if chelant is not used, it is not possible to keep the iron in solution at neutral pH. On the other hand, if an acid pH is used in order to keep iron in solution, the lifetime of the oxidant is remarkably reduced. The presence of EB in the reaction media diminishes the citrate oxidation rate because EB competes with citrate for the hydroxyl radicals.

It was found that the more ethylbenzene in the media, the slower its removal. This fact can be explained taking into account that the Fenton reaction takes place in the aqueous phase, the oxidation rate being limited by the EB concentration in this phase. Increase of hydrogen peroxide improves the EB removal. Using the same reactants, catalyst and pollutant concentrations, higher H_2O_2 conversions are obtained in the slurry system (soil, aqueous and organic phases) than in the liquid system (aqueous and organic phases) due to the unproductive oxidant decomposition in the presence of soil. However, EB conversion was higher in the slurry system, probably due to better contact between aqueous and organic phases in the presence of soil, which enhances the mass transport of EB from the organic to the aqueous phase.

Finally, the ecotoxicity analysis with the microorganism used in the Microtox bioassay indicates that the toxicity of the aqueous

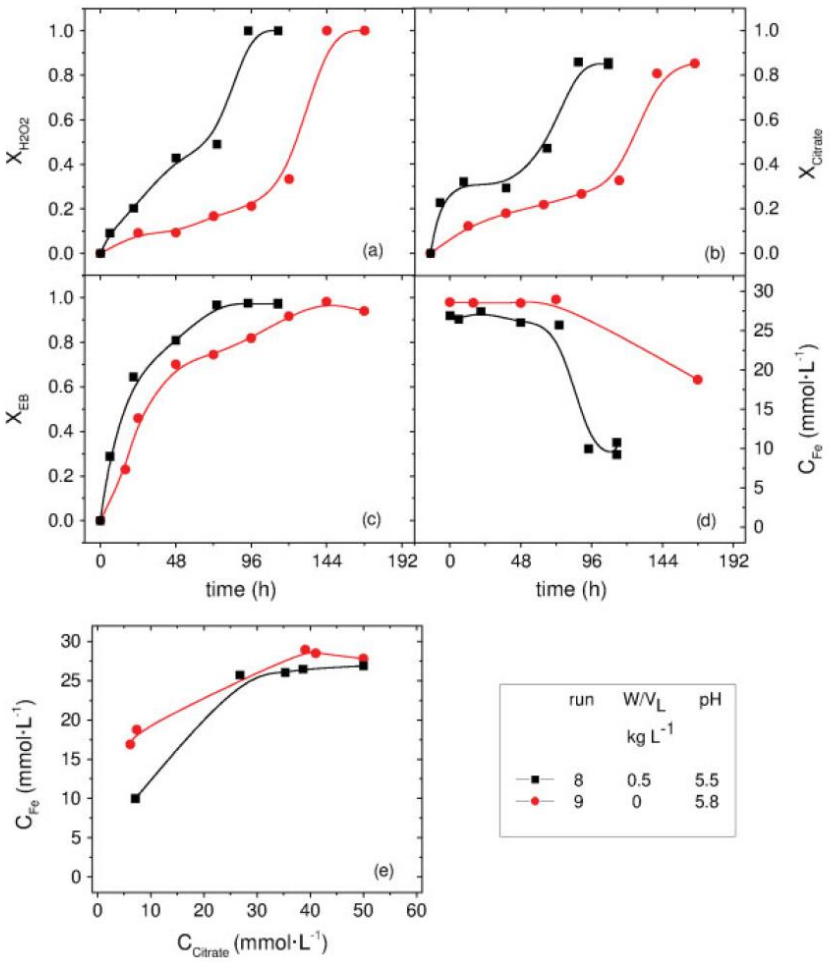

Figure 7. Influence of the presence of soil on the evolution of the reaction media: (a) X_{H2O2} vs t; (b) $X_{Citrate}$ vs t; (c) C_{EB} vs t; (d) C_{Fe} vs t; and (e) C_{Fe} vs $C_{Citrate}$ at 20°C, $V_L/W_{soil} = 2$ mL g^{-1}, $C_{Citrate} = 50$ mmol L^{-1}, $C_{Fe(III)} = 27$ mmol L^{-1}, $C_{EB} = 188$ mmol kg^{-1}, $C_{H2O2} = 1470$ mmol L^{-1}.

phase can be largely related to the EB remaining in this phase. Therefore, nontoxic compounds are released to the aqueous phase during oxidation, under the conditions tested. This indicates the suitability of MFR to remediate NAPL contaminated soils.

ACKNOWLEDGEMENTS

The authors acknowledge financial support from the Comunidad Autónoma de Madrid provided throughout project CARESOIL (S2009AMB-1648) and from Spanish Ministry of Science and Innovation, via project CTM2010-16693.

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4.2 Eliminación de Biodiesel B20

Tras los ensayos de remediación sobre suelo contaminado con etilbenceno, se trabajó con biodiesel B20 como contaminante. Para la eliminación de este tipo de contaminante, compuesto principalmente por hidrocarburos alifáticos procedentes del diesel fósil convencional y por ésteres metílicos de ácidos grasos característicos del biodiesel, se utilizaron Fenton modificado, Fenton like y persulfato activado.

4.2.1 Reactivo Fenton modificado (Artículo 2)

De la misma manera que para la eliminación de etilbenceno, se utilizó el reactivo Fenton modificado añadiendo citrato de sodio tribásico, a una concentración inicial en fase acuosa de 50 mmol·L^{-1}, como agente quelante, como catalizador se utilizó Fe(III) en forma de sulfato férrico ($C_{Fe(III)0}$ = 20 mmol·L^{-1}) y como oxidante peróxido de hidrógeno. Cabe destacar de este estudio que, a diferencia del anterior trabajo, se estudió la eficiencia del reactivo Fenton con y sin agente quelante. Debido a la menor solubilidad en agua del biodiesel con respecto al etilbenceno (Tabla 2.1) y a la oxidación del agente quelante por la aplicación del tratamiento, era bastante probable que la degradación del citrato fuese más rápida que la degradación del propio contaminante. Por tanto, el estudio del efecto del agente quelante en este proceso se consideró un factor crítico a controlar.

Se llevó a cabo el estudio de los diferentes tratamientos a partir de la comparación de las eficiencias de eliminación de las fracciones más representativas del biodiesel B20 así como de la comparación de las variaciones en la huella (*fingerprint*) antes y después de los tratamientos.

Tratamiento Fenton-like sin adición de agente quelante

De estos experimentos, en los que se modificaron las siguientes variables: concentración de hierro $C_{Fe(III)0}$=5 – 20 mmol·L^{-1}, concentración de oxidante $C_{H_2O_20}$ = 2000 - 4000 mmol·L^{-1} y concentración de contaminante, en términos de hidrocarburos totales del petróleo (TPH) (C_{TPH0}= 1000 – 10000 mg·kg^{-1}), se observó que la conversión de oxidante se vio ligeramente afectada, siendo sensiblemente más lenta cuando la concentración de biodiesel B20 en el suelo fue mayor (C_{TPH0} = 10000 mg·kg^{-1}). Por otro

lado se observó un tiempo de reacción muy corto en los tratamientos con $C_{Fe(III)0}$= 20 mmol·L^{-1}, de unas 6 horas aproximadamente, hasta el consumo total de oxidante, consiguiendo unas conversiones de contaminante (expresadas como X_{TPH}, a partir de la determinación de los hidrocarburos totales (TPH) según Ec. [4.7]) que oscilaban entre 69% ($C_{H_2O_20}$ = 2000 mmol·L^{-1}) y 75% ($C_{H_2O_20}$ = 4000 mmol·L^{-1}) para el suelo contaminado con 1000 mg·kg^{-1} de biodiesel B20 y entre 33% ($C_{H_2O_20}$ = 2000 mmol·L^{-1} H_2O_2) y 47% ($C_{H_2O_20}$ = 4000 mmol·L^{-1}) para el suelo contaminado con C_{TPH0} = 10000 mg·kg^{-1}. Como se pudo ver, el aumento en la concentración de oxidante mejoró las conversiones de contaminante en cada uno de los tratamientos.

$$X_{TPH} = \frac{C_{TPH_0} - C_{TPH}}{C_{TPH_0}} \qquad [4.7]$$

Por otro lado, el hierro en disolución, medido como hierro total, disminuyó rápidamente a valores cercanos a los correspondientes a su solubilidad a pH en torno a 2.5 (10 mmol·L^{-1}) (Martí, 2002), en todos los experimentos llevados a cabo. En el experimento con $C_{Fe(III)0}$=5 mmol·L^{-1}, la conversión de biodiesel B20 fue cerca del 60%.

En cuanto a las diferentes fracciones eliminadas de biodiesel B20, se observaron unas mayores conversiones para los FAME, especialmente la del ester metílico del ácido 8,11 octadecadienoico, que para el resto de hidrocarburos alifáticos. Estas mayores eficiencias de eliminación de los FAME se tradujeron en un cambio del *fingerprint* de los contaminantes antes y después del tratamiento.

Tratamiento Fenton modificado con adición de agente quelante

De los experimentos llevados a cabo tras adicionar citrato de sodio se observó que el tiempo de tratamiento se prolongó sustancialmente con respecto a los tratamientos sin agente quelante (en términos promedios, 10 días de tratamiento frente a 6 horas). Sin embargo, se confirmó que el papel del citrato como competidor por el agente oxidante resultó en una disminución en la eficiencia de eliminación del contaminante. La propia oxidación del agente quelante alcanza un punto de inflexión durante el tratamiento, en el que ya no es capaz de quelar todo el catalizador añadido, resultando en un aumento del hierro libre en disolución, acelerando a partir de ese momento la propia oxidación del citrato a partir de X_{CT} = 60%, aproximadamente.

En cuanto a las eficiencias de eliminación del contaminante se observaron las mismas tendencias que cuando no se añadió quelante, es decir, se consiguieron mayores conversiones de biodiesel cuando menor fue su concentración en el suelo y cuando la dosis de agente oxidante fue mayor.

Ensayo de ecotoxicidad

De la misma manera que para la eliminación de etilbenceno, el análisis de la fase acuosa una vez terminada la reacción sirvió para elucidar la presencia de potenciales subproductos de oxidación más tóxicos que los del contaminante de origen. En este sentido, se observó primeramente que, debido a la baja solubilidad de los componentes del biodiesel, las unidades de toxicidad en la fase acuosa eran muy bajas. Sin embargo, se consiguió una disminución de la toxicidad de la fase acuosa tras los tratamientos. Estos ensayos sirvieron para aclarar que tras el tratamiento con el reactivo Fenton modificado no se liberaron especies de mayor potencial tóxico que las iniciales tras el tratamiento.

4.2.2 Persulfato activado (Artículo 3)

De los tratamientos con reactivo Fenton se vio que en ausencia de agente quelante, el tiempo de tratamiento era muy corto, siendo de unas 6 horas aproximadamente para $C_{Fe(III)0}$ = 20 mmol·L^{-1}. Por otro lado, aunque la adición de agente quelante permite prolongar el tiempo de tratamiento (de 6 horas a 10 días aproximadamente), las eficiencias finales de eliminación de contaminante fueron inferiores a las que se obtuvieron cuando no se añadió agente quelante.

Dadas las ventajas del uso del persulfato activado (elevado poder oxidante y alta estabilidad en suelo, entre otras), se estudió la eficacia del persulfato activado para degradar biodiesel B20.

Efecto del agente quelante

Debido a que el persulfato activado con el sistema hierro-ligando ha proporcionado buenos resultados para la eliminación de determinados contaminantes como anilina, naftaleno y tricloroetileno, entre otros (Anotai et al., 2011; Liang et al., 2004; Yan and Lo, 2013), se probó su eficacia para eliminar biodiesel B20, utilizando la

misma concentración de agente quelante que para la eliminación de etilbenceno (C_{CT0} = 50 mmol·L^{-1}). Para las condiciones de trabajo usadas se observaron eficiencias de eliminación muy pequeñas, incluso despreciables, en relación a la eliminación de agente quelante. Tras 4 días de reacción se observó que el mejor resultado fue para el experimento en el que no se añadió citrato de sodio o ácido cítrico. A raíz de este resultado se probó la aplicación de persulfato activado sin agente quelante, con diferentes tipos de activación con hierro como protagonista

Influencia del tipo de activador

Para estudiar la influencia del tipo de activador se utilizó hierro en diversas formas a una misma concentración inicial (20 mmol·L^{-1}). La activación se probó con Fe(II) en forma de sulfato ferroso, con hierro cerovalente granular (gZVI) (dp = 0.32-0.71 mm) y con nanopartículas de hierro cerovalente (nZVI). Los tratamientos se prolongaron durante cerca de 1000 horas (42 días aproximadamente) y se realizó el correspondiente seguimiento de oxidante, hierro en disolución, pH y contaminante con el tiempo de reacción. De los resultados obtenidos se observó que la conversión de oxidante se estabilizó al tiempo final, y que además fue superior cuando se usaron las ZVI (granulares o nano) que cuando se añadió Fe(II). De acuerdo a las ecuaciones [4.8] y [4.9], para poder generar una molécula de radical sulfato (SO_4·), se necesitan dos moléculas de persulfato ($S_2O_8^{2-}$) como resultado de la corrosión del hierro cerovalente por el persulfato. Por otra parte, el pH se mantuvo ácido a lo largo de los 3 distintos tratamientos y la concentración de hierro se fue acercando al valor correspondiente a su solubilidad (10 mmol·L^{-1}). Cuando se añadió Fe(II), la concentración fue disminuyendo progresivamente fruto de la oxidación a Fe(III) y posterior precipitación. En cambio, en el caso del hierro cerovalente, se observó un aumento progresivo hasta un valor cercano a los 10 mmol·L^{-1}.

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + 2\,SO_4^{2-} \qquad [4.8]$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot-} \qquad [4.9]$$

Las eficiencias de eliminación del biodiesel B20 fueron mayores cuando la activación se realizó con ZVI (60% para nZVI, 54% para gZVI) que cuando fue con Fe(II) (X_{TPH} = 30%). De acuerdo a estos resultados y en concordancia con la literatura,

un exceso de Fe(II) puede acabar traduciéndose en un consumo improductivo de persulfato (Liang et al., 2004; Romero et al., 2010; Vicente et al., 2011b), disminuyendo considerablemente su capacidad de actuar sobre el contaminante. Por otro lado, dado que la adición de hierro en forma de nanopartículas permite actuar como una fuente continua de hierro, este consumo improductivo se reduce y permite activar el persulfato durante más tiempo y de una forma más dosificada.

Prueba de inyecciones consecutivas de hierro

Después de comprobar que los mejores resultados se dieron cuando la activación se llevó a cabo con hierro cerovalente en forma de nanopartículas, se probó la adición de nanopartículas en dosis consecutivas con objeto de aprovechar el persulfato que no había reaccionado para intentar conseguir una mayor eficiencia de eliminación del contaminante. Tras esta prueba se observó que, después de 5 adiciones a la inicial, la conversión de contaminante no mejoró sustancialmente. Este hecho dio a entender la presencia de una fracción de biodiesel B20 recalcitrante más difícil de degradar, coincidiendo con la literatura, donde ya se ha indicado las dificultades de conseguir eficiencias de eliminación de diesel por encima del 60% (Liang and Guo, 2012; Yen et al., 2011).

Eliminación de las diferentes fracciones de biodiesel

De la misma manera que para el tratamiento con el reactivo Fenton, se observaron que las fracciones FAME fueron eliminadas más fácilmente que los hidrocarburos alifáticos del diesel fósil convencional. En la Tabla 4.3 se resumen las conversiones finales obtenidas para cada uno de los tratamientos.

Tabla. 4.2. Resumen de las eficiencias de eliminación para cada uno de los diferentes tratamientos llevados a cabo en la aplicación del reactivo Fenton (modificado y like) para la eliminación de biodiesel B20 (20% FAME, 80% diesel). T^a = 20 ºC, sin ajuste previo del pH del medio. W_S = 5 g, V_L = 10 mL, V_L/W_S= 2 mL·g^{-1}. Tiempo máximo de tratamiento: 13 días.

mmol biodiesel promedio (nc16)	C_{TPH0}		$C_{H_2O_20}$		$C_{Fe(III)0}$		C_{CT0}		$X_{alifáticos}^{final}$	X_{FAME}^{final}	X_{TPH}^{final}
	mmol·kg^{-1} promedio (nc16)	***mg·kg^{-1}***	***mmol·L^{-1}***	***mg·L^{-1}***	***mmol·L^{-1}***	***mg·L^{-1}***	***mmol·L^{-1}***	***mg·L^{-1}***			
0.022	4.42	1000	2000	68000	20	1100	0	0	62%	94%	70%
0.022	4.42	1000	4000	136000	20	1100	0	0	66%	94%	75%
0.220	44.2	10000	2000	68000	20	1100	0	0	18%	66%	33%
0.220	44.2	10000	4000	136000	20	1100	0	0	33%	76%	47%
0.022	4.42	1000	2000	13600	5	280	0	0	45%	86%	60%
0.022	4.42	1000	400	68000	20	1100	50	12900	10%	23%	11%
0.022	4.42	1000	2000	68000	20	1100	50	12900	18%	63%	31%
0.022	4.42	1000	4000	136000	20	1100	50	12900	25%	72%	37%
0.220	44.2	10000	2000	68000	20	1100	50	12900	8%	32%	12%

Tabla. 4.3. Resumen de las eficiencias de eliminación para cada uno de los diferentes tratamientos llevados a cabo en la aplicación de persulfato activado para la eliminación de biodiesel B20 (20% FAME, 80% diesel). T^a = 20 ºC, sin ajuste previo del pH del medio. C_{PS0} = 200 mmol·L^{-1}, C_{TPH0} = 1000 mg·kg^{-1}, W_S = 5 g, V_L = 10 mL, V_L/W_S=2 kg·L^{-1}. Tiempo final de tratamiento: 42 días.

Fuente hierro	C_{Fe0}		***Tipo quelante***	C_{CT0}		$X_{alifáticos}^{final}$	X_{FAME}^{final}	X_{TPH}^{final}
	mmol·L^{-1}	***mg·L^{-1}***		***mmol·L^{-1}***	***mg·L^{-1}***			
$Fe_2(SO_4)_3$ Fe (III)	20	1100	Citrato de sodio	50	12900	-	-	~0%
$FeSO_4$ Fe (II)	20	1100	Ácido Cítrico	50	9600	-	-	~0%
$FeSO_4$ Fe(II)	20	1100	Citrato de sodio	50	12900	-	-	~0%
$FeSO_4$ Fe(II)	20	1100	-	-	-	9%	78%	30%
Hierro cerovalente granular	20	1100	-	-	-	34%	84%	54%
Nanopartículas hierro cerovalente	20	1100	-	-	-	39%	85%	60%
Nanopartículas hierro cerovalente	20 +6 dosis de nZVI 20 mmol·L^{-1}	6700	-	-	-	-	-	62%

ARTÍCULO 2/ ARTICLE 2

Título/*Title*: Remediation of a biodiesel blend-contaminated soil by using a modified Fenton process.

Autores/*Authors*: Fernando Pardo, Juana M. Rosas, Aurora Santos, Arturo Romero.

Estado actual/*current status*: Advanced Oxidation Processes For Environmental Protection. Environmental Science and Pollution Research. Noviembre / *November* 2014, 21: 21, 2198-12207.
Recibido/*Received*: 13-01-2014. Aceptado para publicación/*Accepted for publication*: 01-05-2014. Publicado Online/*First Published online*: 17-05-2014.

DOI: 10.1007/s11356-014-2997-2

Factor de impacto/Impact factor (JCR, 2014): 2.828

Environ Sci Pollut Res
DOI 10.1007/s11356-014-2997-2

ADVANCED OXIDATION PROCESSES FOR ENVIRONMENTAL PROTECTION

Remediation of a biodiesel blend-contaminated soil by using a modified Fenton process

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Received: 13 January 2014 / Accepted: 1 May 2014

Abstract A soil contaminated with a B20 biodiesel blend (20 % biodiesel, 80 % diesel) has been treated by modified Fenton process with or without chelant addition. All experiments were conducted without pH adjustment. The reagents used were as follows: hydrogen peroxide as oxidant (400–4,000 mmol L^{-1}), ferric ion as catalyst (5–20 mmol L^{-1}), and trisodium citrate (50 mmol L^{-1}) as chelating agent. Soil was spiked at two different pollutant concentrations (1,000–10,000 mg diesel kg^{-1} soil). Higher total petroleum hydrocarbon (TPH) removal efficiencies were obtained (up to 75 %) after the treatment in the absence of the chelant due to the low pH obtained in this case. In the presence of chelant, the TPH conversion obtained was lower because both higher pH is obtained and chelant competes with diesel for the oxidant. On the other hand, at neutral pH, the lifetime of the oxidant was increased. Fatty acid methyl esters (FAMEs) are easier to remove than diesel aliphatic hydrocarbons from the blend. An important decrease of the aqueous phase toxicity was observed after the modified Fenton reaction, supporting that nontoxic by-products were released to the aqueous phase during the treatment.

Keywords Modified Fenton · Soil remediation · Diesel/biodiesel fractions · Ecotoxicity

Introduction

The vast volume of petroleum products used nowadays becomes then a major environmental and health concern (Pinedo et al. 2013). Soil and groundwater pollution by petroleum products can be caused by accidental spills and leaks from underground storage tanks or pipelines and/or derived from activities such as oil exploitation, smelting, oil transportation, and oily wastewater discharge and irrigation (Tang et al. 2012). Petroleum products (gasoline, diesel, fuel oil…), when present in soil, can reach the water-saturated zone, resulting in a dual problem of soil and groundwater contamination (Newell et al. 1995).

Fenton process, one of the most popular among all in situ chemical oxidation (ISCO) techniques, is based on the interaction of hydrogen peroxide with a soluble catalyst (Fe (II) or Fe (III) salts) to generate highly active oxidative species (•OH, redox $E°$=2.73 V), capable of oxidizing a wide range of organic compounds. The use of Fenton reagent in soil remediation presents the drawbacks that its optimal pH is around 3, and furthermore, hydrogen peroxide moves no longer than 3–4 m and often decomposes within 1–2 m of the injection well (Watts and Teel 2005). Subsequent problems are the precipitation of Fe (II) to $Fe(OH)_3$ at near-neutral pH, leading to problems of injection-well plugging and loss of catalyst (Watts and Teel 2006).

The application of Fenton's chemistry in soils at near-neutral pH (Watts and Teel 2005; Lewis et al. 2009) requires the use of chelating agents, allowing to keep catalyst in solution (Jho et al. 2012; Sun and Pignatello 1992; Venny et al. 2012; Vicente et al. 2011). In several studies, the effectiveness of the modified Fenton by chelating agents has been confirmed in the treatment of a wide variety of contaminated soils with herbicides (Vicente et al. 2012), PAH (Venny et al. 2012), chlorinated hydrocarbons (Cai et al. 2012), and BTEX (Zhao et al. 2011). However, the use of stabilizers or chelating agents was scarcely considered for the remediation of diesel- or fuel oil-contaminated soils (Watts and Dilly 1996), and only some publications have appeared in the last years considering their use (Chang et al. 2013; Xu et al. 2011).

Responsible editor: Philippe Garrigues

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Published online: 17 May 2014

In this sense, some disadvantages must be considered in the use of chelating agents, as for example, the possible oxidation of these compounds. Chelant and pollutant can compete for the hydroxyl radicals with a significant loss of efficiency in the process. This aspect has not been deeply analyzed in the literature, where attention is only paid to the pollutant abatement in the contaminated soil. Nevertheless, previous studies in aqueous phase (Rastogi et al. 2009; Sillanpaa et al. 2011) show that organic chelants are easily oxidized by the hydroxyl radicals.

On the other hand, the few studies of remediation of soil polluted by diesel fractions have been carried out by using mainly fossil fuels (Kong et al. 1998; Tsai and Kao 2009; Villa et al. 2010; Watts and Dilly 1996; Yen et al. 2011), and only few papers are available about remediation of biodiesel-contaminated media, particularly, water contamination (Mitre et al. 2013), but to our best knowledge, no studies of contaminated soils have been carried out. Biodiesel, which is derived from vegetable oils or animal fats, is composed of monoalkyl esters of long-chain fatty acids such as lauric, palmitic, stearic, oleic, etc. Furthermore, toxicity and potential risks of diesel fuel to human exposure are well reported (US department of human health 1995), but only few works have analyzed the possible harmful effects of biodiesel blends in soil (Leme et al. 2012; Restrepo-Florez et al. 2013). In this sense, Leme et al. (2011) observed that biodiesel blends showed genotoxic and mutagenic effects on certain microorganisms in soil systems. In addition, diesel abatement is usually measured as a global value, as total petroleum hydrocarbons (TPHs). However, the different fractions of diesel/biodiesel have different reactivity to the Fenton reagent, being this aspect scarcely studied in the literature.

Therefore, the aim of this work is the study of the remediation of a biodiesel blend contaminated soil by using a modified Fenton process with chelant addition and a conventional Fenton process without chelant addition. The effect of hydrogen peroxide, iron, and pollutant concentration on the evolution of the oxidant, contaminant, and remaining Fe (III) in solution were analyzed. Trisodium citrate (CT) has been used in this work as a chelating agent because this compound is biodegradable and produces a buffer effect, avoiding the acidification of the media, thus increasing the lifetime of the oxidant (Rosas et al. 2014; Vicente et al. 2011). Chelant consumption was also determined when this compound was added.

Furthermore, the diesel abatement was studied not only as TPHs decrease but also examining the removal of the different diesel/biodiesel fractions. Finally, ecotoxicity of the aqueous phase after treatment were determined by using the Microtox bioassay in order to evaluate the possible toxic by-products released to the aqueous phase during the remediation by modified Fenton.

Materials and methods

Reagents

All the reagents used in the experiments were of analytical grade, except commercial biodiesel/diesel blend, which was obtained from a road gas station. Reactions were conducted by using H_2O_2 >30 % (*w*/*w*) from Fisher Chemical, ferric sulfate from Panreac as the catalytic Fe (III) specie, and sodium citrate 2-hydrate ≥99.0 %, from Sigma–Aldrich, as a chelating agent. For the determination of H_2O_2, sulfuric acid >95 %, from Fisher Chemical, and potassium permanganate 99.5 %, from Panreac, were used. Nitric acid 69.5 %, obtained from Scharlau, was utilized as iron ions stabilizer in MP-AES analysis. For the analysis of citrate by HPLC, phosphoric acid ≥85 % and potassium phosphate monobasic ≥99.5 %, purchased from Sigma–Aldrich, were used as mobile phase components. Ultrapure laboratory grade water (MilliQ) obtained from a deionizing system was employed for the preparation of all solutions. Methanol in supragradient HPLC grade, from Fisher Chemical, was used as a quenching agent of the oxidation reactions at intermediate times. Acetone 99.8 % HPLC gradient grade from Fisher Chemical, *n*-hexane 99 % HPLC grade from Scharlab, and dichloromethane 99.8 % HPLC gradient from Sigma–Aldrich were used in the diesel extraction from soil samples. Sodium sulfate anhydrous 99 %, from Fisher Chemical, was employed for the conditioning of soil reaction samples.

Diesel fingerprint characterization

Figure 1 shows the fingerprint of the fuel used as contaminant, which corresponds to a B20 biodiesel blend. The presence of different fatty acid methyl esters (FAMEs), such as hexadecanoic acid (palmitic acid) methyl ester (C17), 8, 11 octadecadienoic acid methyl ester (C19), and 8 octadecenoic acid methyl ester was detected. The sum of the areas of identified FAME is about 20 % of the total sum of areas.

Soil spiking

A sandy clay loam BT horizon from the Autonomous Community of Madrid with neutral pH was selected for this work. The characterization procedure of this soil was described elsewhere (Vicente et al. 2012). The most important soil properties are listed in Table 1.

The spiking of the soil was carried out by adding 500 mL of a contaminant solution (2 or 20 g L^{-1} in *n*-hexane) on 1 kg of clean soil in order to achieve 1,000 and 10,000 mg kg^{-1} of pollutant in soil, respectively. Spiked soil was placed in an orbital shaker for 24 h to ensure homogeneity and after shaking was settled in a fume hood for 48 h to evaporate *n*-hexane.

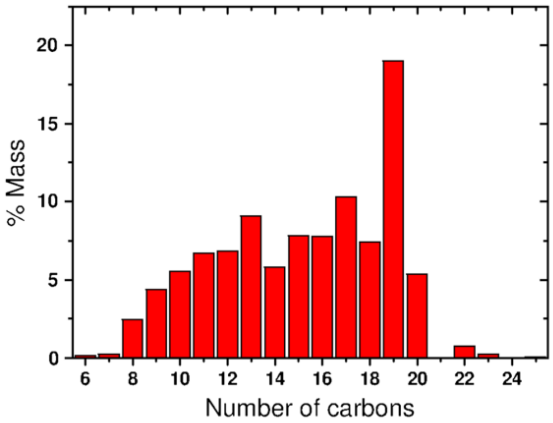

Fig. 1 Fingerprint of the diesel/biodiesel blend sample used in the experiments

Remediation runs

Experiments were conducted without pH adjustment, using 50-mL PTFE centrifuge tubes with PTFE screw cap as batch reactors, stirred isothermally (20 °C) in an orbital shaker (Unitronic Orbital by Selecta) at 100 rpm. Five grams of polluted soil were treated with 10 mL (V_L/W_S=2 mL g^{-1}) of aqueous solution of the reagents (hydrogen peroxide, iron sulfate, sodium citrate). Each reaction tube represents one time point. At the selected time, 10 mL of *n*-hexane/dichloromethane (1:1) were added to the reaction media, and then, the slurry was centrifuged for 10 min at 10,000 rpm with a Meditronic-BL (Selecta), obtaining three differentiated phases. Organic phase was withdrawn and analyzed by GC-FID; the aqueous supernatant was separated from the soil and then, reaction was quenched with 5 mL of methanol. Previous to this quenching step, the pH was evaluated. The remaining H_2O_2, citrate, and total iron concentrations in the aqueous phase were also analyzed. It was confirmed that methanol did not interfere in H_2O_2 analysis. Finally, soil phase was treated with 5 g of anhydrous sodium sulfate to eliminate moisture and to disperse the solid particles. Afterwards, Soxhlet extraction with *n*-hexane/acetone (1:1) (EPA method 3540C) was used for the analysis of the remaining diesel by gas chromatography (GC)-flame ionization detection (FID) and GC-mass spectrometry (MS). Duplicate tests were performed for each experiment and the average value was used for figures with an experimental error lower than 5 %. Besides, some reactions were conducted in triplicate for the analysis of total organic carbon (TOC) and ecotoxicity in the aqueous phase at the final time reaction, when all H_2O_2 was consumed. The experiments carried out are summarized in Table 2.

Table 1 Properties of the soil used for the remediation experiments (standard deviation=4–7 %)

Soil organic mater (SOM), %		0.365
Total organic carbon (TOC), %		0.196
SOM fractions, %	Labile pool I	0.114
	Labile pool II	0.012
	Recalcitrant	0.07
Total carbon (TC), %		0.198
Inorganic carbon (IC), %		0.002
pH		7.22
Apparent surface area (Sg^{BET}) m^2 g^{-1}		23
Pore volume cm^3 g^{-1}		0.031
[Mn] mg g^{-1}		0.170
[Fe] mg g^{-1}	Total	18.2
	Amorphous	0.525
	Crystalline	6.710

Analytical method

For quantitative analysis of diesel a GC with FID (HP 6890) and equipped with a capillary DB-1 column (30 m×0.25 mm i.d.×1 μm) was used. The diesel concentration was determined by the sum of the total peak area (EPA method 8015B). The chromatographic conditions used were as follows: injector temperature, 280 °C; detector temperature, 330 °C; and carrier gas (He) flow rate, 10 mL min^{-1}. The analysis was performed with an initial oven temperature 45 °C, followed by a first ramp of 12 °C min^{-1} to 250 °C and a second ramp of 8 °C min^{-1} to 325 °C. The final run time was 46.46 min.

Diesel compounds were identified by GC/MS (HP 6890N MSD 5975B); a HP-5 column (30 m×0.32 mm i.d.×0.25 μm) was used for the analysis. The same chromatographic conditions were used in GC/MS and GC/FID.

For citrate determination, a buffer solution with 20 mmol L^{-1} $H_2P_2O_4$, acidified to pH=2.1 with phosphoric

Table 2 Experimental conditions for runs carried out in batch tests. *T*= 20 °C

Run	H_2O_2 (mmol L^{-1})	Fe III (mmol L^{-1})	Citrate (mmol L^{-1})	Diesel (mg kg^{-1})	*W* soil (g)	*V* liquid (mL)
1	2,000	20	0	1,000	5	10
2	4,000	20	0	1,000		
3	2,000	20	0	10,000		
4	4,000	20	0	10,000		
5	2,000	5	0	1,000		
6	400	20	50	1,000		
7	2,000	20	50	1,000		
8	4,000	20	50	1,000		
9	2,000	20	50	10,000		
10	2,000	0	0	0		
11	2,000	0	50	0		

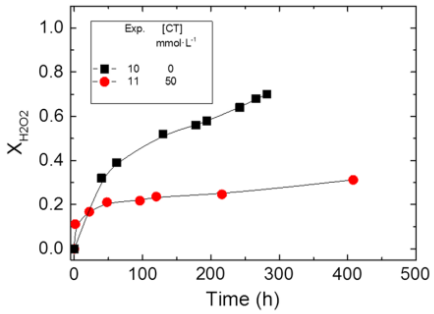

Fig. 2 Comparison of H_2O_2 lifetime alone and with the addition of chelant (50 mmol·L^{-1} citrate at 20°C, V_L/W_{soil}=2 mL g^{-1}, $C_{Fe(III)}$= 0 mmol L^{-1}

acid, was used and a flow rate of 0.2 mL min^{-1}. The programed temperature of the column during analysis was 20°C. Reaction samples were prepared by adding 0.9 mL of buffer phosphate mobile phase to 0.1 mL of quenched reaction sample. A Poroshell 120 SB-C18 in 2.1 mm×100 mm and 2.7 μm of particle size column was used.

The concentration of H_2O_2 in solution was determined by titration with a solution of potassium permanganate, $KMnO_4$, of known concentration, in sulfuric acid by using a potentiometric titration analyzer supplied by Metrohm. pH was measured with a pH glass electrode also supplied by Metrohm.

Analysis of iron was carried out with a microwave plasma-atomic emission spectrometer 4100 MP-AES (Agilent Technologies); a OneNeb nebulizer was used. Sample, previously acidified with 1 % (*v*/*v*) HNO_3, was fed into the MP-AES with a peristaltic pump operating at 8 rpm. The selected wavelength for iron determination was 259.94 nm.

The TOC content in the aqueous phase was measured by a Shimadzu TOC-V CSH analyzer, as described in the standard procedure EN 13137. The toxicity of the aqueous supernatant was determined by the standard Microtox test procedure (ISO 11348-3, 1998) (Romero et al. 2008), by using a Microtox M500 analyzer (Azur Environmental). This standard test is based on the decrease of light emission by Photobacterium phosphoreum resulting from the exposure to a toxicant. The microorganisms were Microtox Acute Reagent (Vibrio Fischeri) supplied by I.O. Analytical.

Results and discussion

Soil treatment using Fenton-like without the addition of chelating agent

Prior to remediation runs, it was confirmed that the presence of chelating agent minimized nonproductive consumption of hydrogen peroxide, as shown in Fig. 2.

Different runs have been performed by using two different H_2O_2 initial concentrations (2,000 and 4,000 mmol L^{-1}, respectively) and two diesel concentrations (1,000 and 10,000 mg kg^{-1}, respectively). The initial iron concentration in solution has been fixed to 20 mmol L^{-1} in each experiment and the chelating agent was not added (acidic pH was obtained after addition of 20 mmol L^{-1} iron). Figure 3 shows the evolution of pH and the species involved in the slurry reaction (H_2O_2, iron, and TPH). It can be seen that pH is barely influenced by the contaminant or oxidant concentration. A slight increase of pH was noticed at the final reaction times,

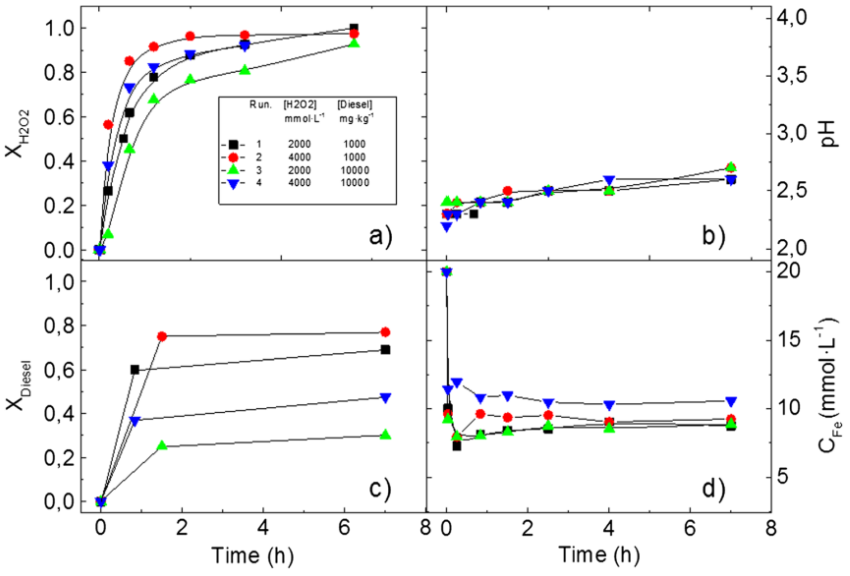

Fig. 3 Evolution of the reaction media without addition of citrate. **a** X_{H2O2} vs *t*. **b** pH vs *t*. **c** X_{Diesel} vs *t*. **d** C_{Fe} vs *t*. At 20°C, V_L/W_{soil}= 2 mL g^{-1}, $C_{Citrate}$=0 mmol L^{-1}, $C_{Fe(III)}$=20 mmol L^{-1}

which can be explained by the release of solved CO_2 from the aqueous phase during the mineralization of the pollutant (Ndounla et al. 2014).

The total amount of iron in solution decays quickly at initial times, due to its partial precipitation, and then about 10 mmol L^{-1} of iron remains constant during reaction, in agreement with the value of Fe (III) solubility at pH=2.5 reported by Burriel et al. (1985).

Regarding to the time evolution of H_2O_2, it can be seen that the oxidant has a short lifetime in the absence of chelating agents (about 90 % of the oxidant has been consumed at $t<$ 4 h, in runs 1 to 4). On the other hand, a slower rate of the oxidant consumption is noticed as diesel concentration in soil increases (using the same oxidant dosage), in agreement with the results reported in literature (Li et al. 2007). This trend could be associated to a decrease of the unproductive consumption of hydroxyl radical by reaction with the oxidant in the presence of diesel. Besides, the oxidant conversion becomes lower as the initial oxidant concentration decreases, when the same pollutant concentration in soil is used.

TPH removal was between 75 and 69 % for the soil contaminated with 1,000 mg kg^{-1}, while lower removal percentages (TPH conversions between 47 and 33 %) were obtained for the soil with 10,000 mg kg^{-1} of diesel. The increase of the oxidant dosages from 2,000 to 4,000 mmol L^{-1} produced an increase in the diesel conversion (as TPH), this effect being more pronounced at the higher diesel concentration used. As can be seen in Fig. 3, the TPH conversion increases quickly at the initial reaction times, achieving a plateau as the oxidant is consumed.

In Fig. 3, the TPH conversion has been only shown. However, the effect of the remediation carried out on the different diesel/biodiesel blend fractions can be diverse. In this sense, a classification of the most representative components found in this diesel fingerprint is shown in Table 3, considering a range of number of carbons between 14 and 22. Once these components are known, the effect of the remediation treatment on the conversion of each fraction, in runs 1 to 4, is shown in Fig. 4. For the sake of comparison, the results obtained in an additional experiment (run 5 in Table 2), which consisted of the treatment of 1,000 mg kg^{-1} diesel-contaminated soil, with 2,000 mmol L^{-1} H_2O_2 and 5 mmol L^{-1} Fe (III), have been also included. As can be seen in Fig. 4, the highest conversion is obtained for the diesel fractions with 17 and 19 carbon compounds, corresponding to the following FAME, hexadecanoic acid methyl ester (17 C), and the couple 8,11 octadecadienoic acid methyl ester with 8, octadecenoic acid methyl ester, both with 19 carbons (Table 4). Furthermore, an increase of the pollutant removal at high iron and oxidant dosages can be observed in this figure, in agreement with other results reported in the literature (Tsai and Kao 2009; Watts and Dilly 1996). Finally, Fig. 5 shows a comparison between the fingerprint of the diesel blend before and after the treatment, supporting the fact that FAMEs are easier to degrade than diesel aliphatic hydrocarbons (tetradecane, pentadecane, hexadecane, etc.).

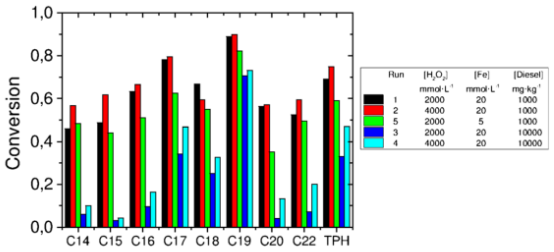

Fig. 4 Conversion of the different diesel fractions, from C14 to C22, in the experiments conducted without citrate addition. T=20°C, V_L/W_{soil}= 2 mL g^{-1}

Modified Fenton-like reaction with chelating agent

Because of the short lifetime of the oxidant noticed in the absence of chelant, three additional experiments have been carried out by adding 2,000 mmol L^{-1} H_2O_2, 20 mmol L^{-1} in

Table 3 Most representative compounds found in the spiked soil

Compound	Number of carbons	w, %
Tetradecane	14	4.76
Pentadecane	15	6.85
Hexadecane	16	12.40
Heptadecane	17	13.70
Hexadecanoic acid methyl ester	17	13.26
Octadecane	18	12.24
Nonadecane	19	4.85
8,11-Octadecadienoic acid Methyl ester	19	24.22
9-Octadecenoic acid (Z) methyl ester	19	
Eicosane	20	4.03
Docosane	22	3.69

Table 4 Conversion of C17 and C19 compounds in the experiments carried out without citrate addition

	Experiments				
	1	3	2	4	5
Hexadecanoic acid ME	0.948	0.456	0.949	0.681	0.847
Heptadecane	0.620	0.223	0.648	0.246	0.410
8,11 Octadecadienoic acid ME 9, Octadecenoic acid ME	0.935	0.823	0.938	0.843	0.898
Nonadecane	0.660	0.056	0.698	0.116	0.448

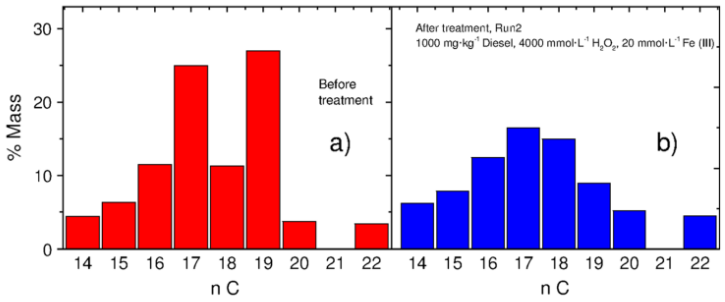

Fig. 5 Diesel fingerprint (C14 to C22) before and after (run 2, X_{Diesel}=0.75) the treatment with Fenton like

Fe (III), and 50 mmol L^{-1} of trisodium citrate (CT), in accordance with Vicente et al. (2011), in which the same concentration of chelant was used, in order to extend the lifetime of H_2O_2. Soils with different diesel B20 concentrations (0, 1,000, and 10,000 mg kg^{-1}) were tested. The results obtained in the presence of chelant are shown in Fig. 6. As can be seen, the contaminant concentration does not produce any influence on the pH evolution (Fig. 6b) during the reaction. Besides, as aforementioned, an increase of pH was observed at the final reaction times which can be explained by the release of CO_2 from the mineralization of the organic compounds, which is solved in the media. Furthermore, it can be noticed only a slight influence of the contaminant concentration on the hydrogen peroxide conversion.

The chelating agent concentration decreases during the course of the reaction (as it is shown in Fig. 6e), which results

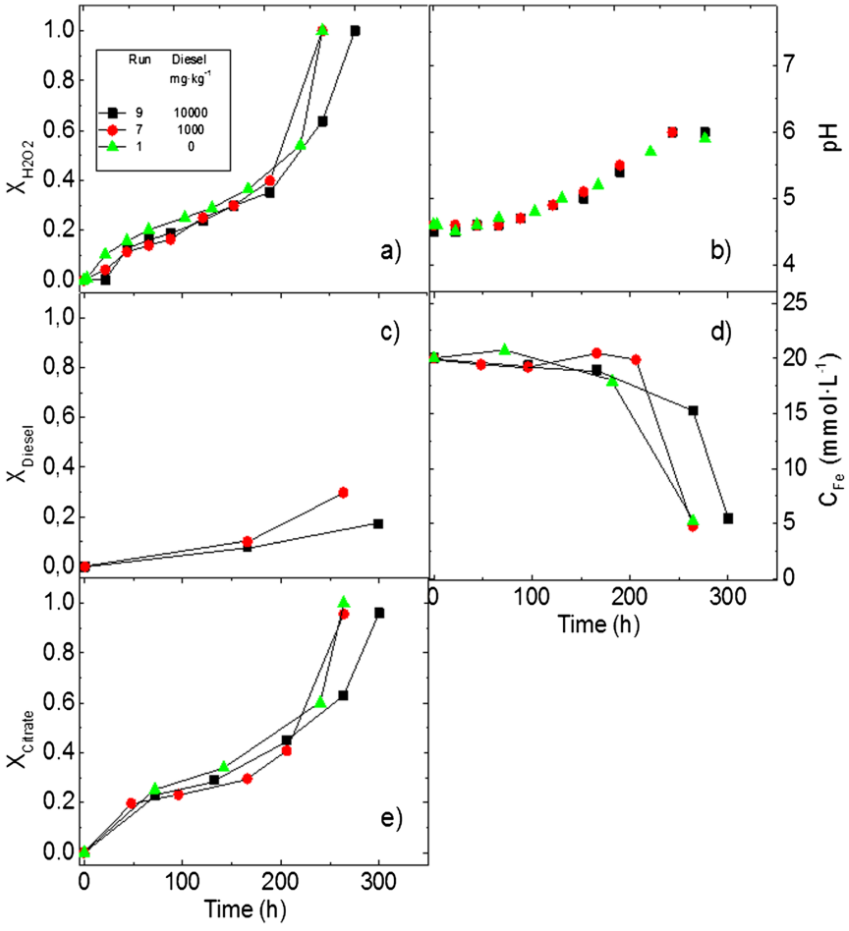

Fig. 6 Evolution of the reaction media with addition of citrate, influence of diesel concentration. **a** X_{H2O2} vs *t*. **b** pH vs *t*. **c** X_{Diesel} vs *t*. **d** C_{Fe} vs *t*. **e** $X_{Citrate}$ vs *t*. At 20°C, V_L/W_{soil}=2 mL g^{-1}, $C_{Citrate}$=0 mmol L^{-1}, $C_{Fe(III)}$= 20 mmol L^{-1}

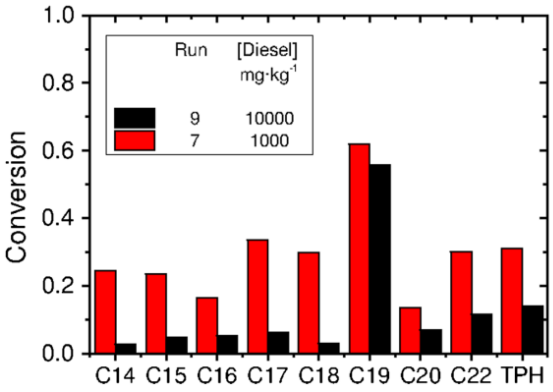

Fig. 7 Conversion of the different diesel fractions, from C14 to C22, in the experiments with citrate addition, influence of diesel concentration. T=20°C, V_L/W_{soil}=2 mL g^{-1}

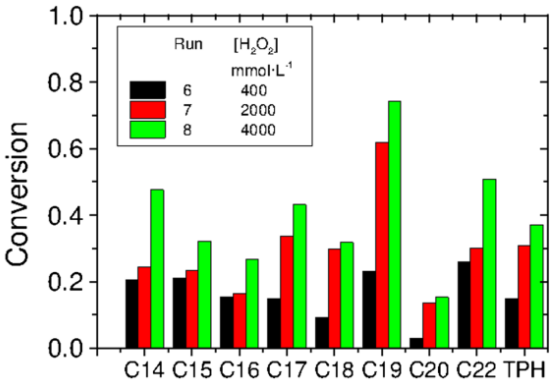

Fig. 9 Conversion of the different diesel fractions, from C14 to C22, in the experiments with citrate addition, influence of oxidant concentration. T=20°C, V_L/W_{soil}=2 mL g^{-1}

in that CT competes with the pollutant for the oxidant. This scavenging reaction could explain the lower diesel conversion obtained with CT, in relation to the one found in absence of the chelant. If the reaction takes place in the aqueous phase, the lower the solubility of the organic pollutant the higher the oxidant scavenging by the chelant. The lower TPH conversion is also due to the higher pH obtained when CT is added as chelant. The amount of free Fe (III) is expected to be lower than that corresponding to the absence of chelant, as previously reported in literature (Feng et al. 2012; Xue et al. 2009).

On the other hand, due to the relationship between total iron and chelating agent in solution (Vicente et al. 2012), iron

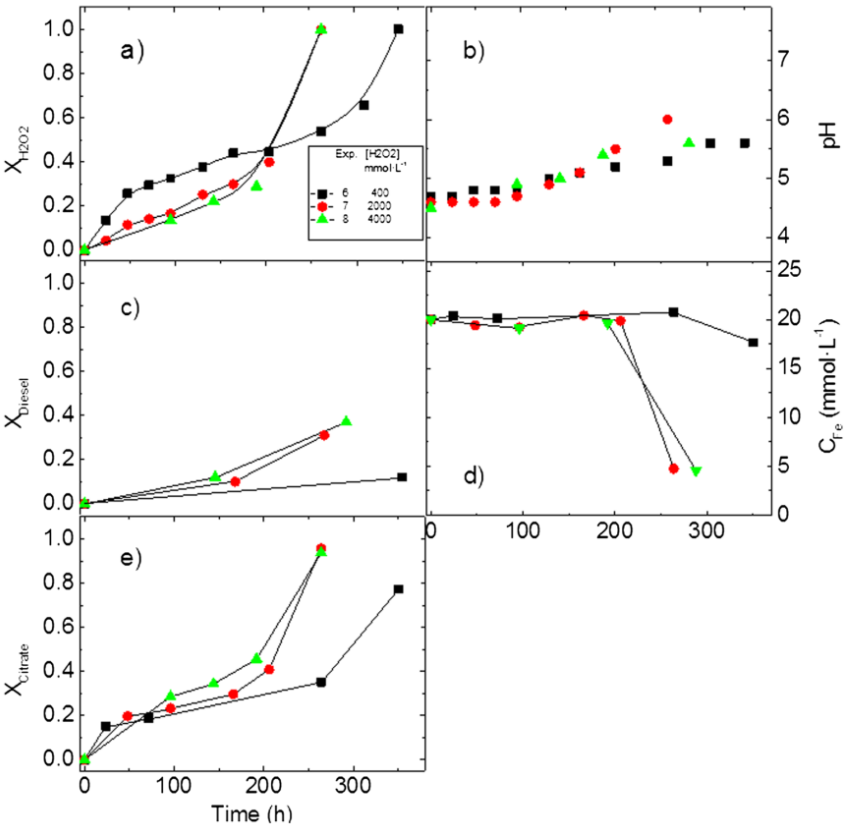

Fig. 8 Evolution of the reaction media with citrate, influence of diesel concentration. **a** X_{H2O2} vs t. **b** pH vs t. **c** X_{Diesel} vs t. **d** C_{Fe} vs t. **e** $X_{Citrate}$ vs t. At 20°C, V_L/W_{soil}= 2 mL g^{-1}, $C_{Citrate}$=0 mmol L^{-1}, $C_{Fe(III)}$=20 mmol L^{-1}

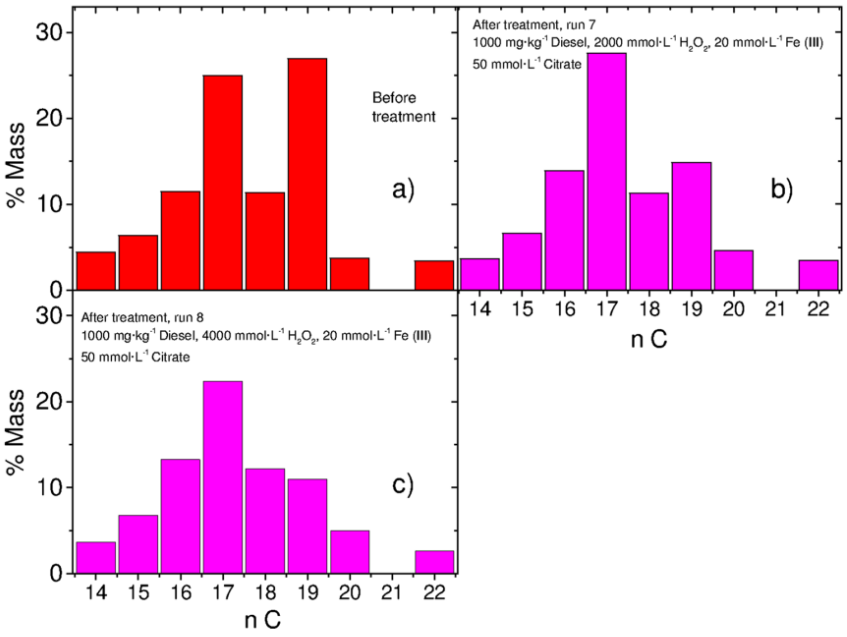

Fig. 10 Fingerprints of diesel (C14 to C22) before and after (run 7, X_{Diesel}=0.31; run 8, X_{Diesel}= 0.37) the treatment with modified Fenton

in solution decreases, as a result of its precipitation, when citrate is consumed, which explains the tendency noticed in Fig. 6d.

Besides, an S-shape curve is observed in Fig. 6 for oxidant and chelant consumption. The inflection point corresponds to a CT conversion about 60 %. Above this value, the remaining CT is not able to chelate all the Fe (III) added and Fe (III) free increases, producing a rise in the rates of CT oxidation and oxidant consumption.

Figure 7 shows the conversion of the different diesel fractions in the presence of citrate and at different diesel concentrations. In the same way that it was noticed in absence of CT, the conversion of diesel in the soil was higher when the concentration of contaminant is lower. Regarding to the elimination of the different diesel fractions, it was observed that the highest conversion corresponded to the C19 fraction in both cases (1,000 and 10,000 mg kg^{-1} diesel).

Table 5 Conversion of C17 and C19 compounds in the experiments carried out with citrate addition

	Experiments			
	6	7	9	8
Hexadecanoic acid ME	0.186	0.337	0.092	0.562
Heptadecane	0.115	0.139	0.018	0.307
8,11 Octadecadienoic acid ME 9, Octadecenoic acid ME	0.277	0.733	0.640	0.857
Nonadecane	0.010	0.049	0.003	0.169

To study the influence of H_2O_2 concentration on the soil remediation in the presence of chelant (CT), different experiments fixing the iron and citrate concentrations and at different oxidant concentrations were carried out. The corresponding results obtained by adding 20 mmol L^{-1} Fe III, 50 mmol L^{-1} citrate, and 400–2,000–4,000 mmol L^{-1} H_2O_2, respectively, to a soil polluted with 1,000 mg kg^{-1} diesel are shown in Fig. 8. As can be seen, the time evolution of pH is slightly affected by the oxidant concentration. The increase in the hydrogen peroxide dosage produces a slight rise in the chelant oxidation, as it is shown in Fig. 8e. The concentration of total iron in solution is related to the CT conversion, an iron precipitation is noticed at CT conversions above 60 % (Fig. 8d, e). Again, S-shape curves for oxidant and citrate conversions as a function of time are observed in runs 6, 7, and 8.

Table 6 Removal efficiency of aliphatic and FAME-identified compounds, respectively, in all runs

Run	$X_{Aliphatic}$	X_{FAME}
1	0.62	0.94
2	0.66	0.94
3	0.18	0.66
4	0.33	0.76
5	0.45	0.86
6	0.10	0.23
7	0.18	0.63
8	0.08	0.32
9	0.25	0.72

A relatively high TPH removal (about 37 %) was achieved at the highest H_2O_2 used (4,000 $mmol^{-1}$). On the other hand, the lowest diesel conversion (about 12 %) was obtained with 400 mmol L^{-1} H_2O_2. The effect of the oxidant dosage on the different fractions of the diesel is shown in Figs. 9 and 10. It is also observed that among methyl ester compounds, the group 8, 11 octadecadienoic/9 octadecenoic acid methyl esters are degraded earlier than the hexadecanoic acid methyl ester (C17). The results obtained for the main compounds identified in diesel at the final reaction times, in runs 6 to 9, are shown in Table 5, confirming the higher reactivity of the FAME compounds. Finally, in Table 6, the corresponding removal efficiencies of aliphatic compounds and FAME are shown, respectively, of each run.

Ecotoxicity assay

Ecotoxicity analysis of the aqueous phase at the final reaction time (300 h) was measured in runs 7 (1,000 mg diesel kg^{-1} soil) and 9 (10,000 mg diesel kg^{-1} soil). This long time was selected to ensure a total consumption of H_2O_2. Toxicity Units (TUs) of 13.1 and 36.7 were obtained, respectively.

For the sake of comparison, TUs of the aqueous phase were measured after contact during 48 h of 5 g of soil contaminated with 1,000 or 10,000 mg kg^{-1} diesel, with 10 mL of an aqueous solution with 50 mmol L^{-1} of citrate and 20 mmol L^{-1} of Fe (III), without the addition of the oxidant. A value of 93.9 TUs for the sample with 10,000 mg kg^{-1} diesel in soil and a value of 83.2 TUs for the sample with 1,000 mg kg^{-1} diesel in soil were obtained, respectively. Similar values of TUs are obtained for the aqueous phases in the absence of oxidant because the diesel solubility in the aqueous phase is not expected to change with the diesel concentration in soil. As can be seen, an important reduction of the TUs is observed with the addition of the oxidant, a decrease of 86 % TUs in run 7 and 56 % in run 9, respectively. These results are in concordance with others reported in the literature, where a decrease in ecotoxicity after treatment of hydrocarbon contaminated soils was also observed by using bioremediation (Molina-Barahona et al. 2005) or ozonation (Shin et al. 2005). These low values of TUs obtained in the aqueous phase of the treated soils with modified Fenton reaction indicate that toxic intermediates are not released to this phase during the soil remediation by modified Fenton.

Conclusions

The remediation of a B20 biodiesel blend-contaminated soil by using modified Fenton process has been studied. If chelating agent is not added, in real applications, the pH of the media must keep acid to avoid iron precipitation. At these acid conditions, a high TPH removal efficiency is obtained (up to 75 %) but the lifetime of the oxidant is short. When trisodium citrate (CT) is added as chelant, the oxidant is stabilized but the TPH conversion obtained is lower because of both the higher pH achieved and the competition of pollutant and chelant for the oxidant. In both cases (adding or not the chelating agent) the highest effectiveness were obtained in the removal of C19 FAME compounds, while the aliphatic carbon chains show lower reactivity. In terms of toxicity, aqueous phases are less toxic after the treatment. Therefore, nontoxic by-products are released to the aqueous phase in the Fenton treatment.

Acknowledgments The authors acknowledge financial support from the Comunidad Autonomy de Madrid provided throughout project CARESOIL (S2009AMB-1648) and from the Spanish Ministry of Science and Innovation, project CTM2010-16693.

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ARTÍCULO 3/ ARTICLE 3

Título/*Title*: Remediation of a Biodiesel Blend-Contaminated Soil with Activated Persulfate by Different Sources of Iron.

Autores/*Authors*: Fernando Pardo, Juana M. Rosas, Aurora Santos, Arturo Romero.

Estado actual/*current status*: Water, Air, & Soil Pollution. Febrero / *February* 2015. 226:17.
Recibido/*Received*: 01-08-2014. Aceptado para publicación/*Accepted for publication*: 05-12-2014. Publicado Online/*First Published online*: 05-02-2015.

DOI: 10.1007/s11270-014-2267-4

Factor de impacto/Impact factor (JCR, 2014): 2.349

Water Air Soil Pollut (2015) 226: 17
DOI 10.1007/s11270-014-2267-4

Remediation of a Biodiesel Blend-Contaminated Soil with Activated Persulfate by Different Sources of Iron

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Received: 1 August 2014 / Accepted: 5 December 2014 / Published online: 5 February 2015

Abstract The present work studies the remediation of a B20 (20 % biodiesel, 80 % diesel) biodiesel blend-contaminated soil (1,000 mg kg^{-1}) with persulfate activated by iron. Three different sources of iron (Fe(II)), granular zerovalent iron (gZVI), and a slurry of nanoparticles of zerovalent iron (nZVI), without pH adjustment were tested. Besides, the effect of the addition of chelating agents, such as trisodium citrate (SC), or citric acid (CiA), has been also studied. SC promotes pH under near-neutral conditions and reaction takes place at low rate at these experimental conditions. On the other hand, the use of CiA leads to an acidic pH and chelating agent is oxidized at higher rate than total petroleum hydrocarbons (TPH). Therefore, CiA addition does not seem to produce any improvement on the removal efficiency of TPH. Regarding the three different sources of iron used as activators, Fe(II), gZVI and nZVI, in absence of chelating agent, under acidic pH and by adding the same amount of iron, the highest TPH conversion was obtained with ZVI (about 60 %), while a conversion of about 40 % was obtained with the addition of Fe(II). The maximum TPH conversion value was achieved in shorter time using nZVI. Concerning the removal efficiency of each fraction of biodiesel abated, fatty acid methyl esters (FAME) were by far the easiest to oxidize, achieving 100 % of conversion, either by using Fe(II) or nZVI activated persulfate.

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Keywords Soil remediation · Biodiesel · ISCO · Activated persulfate

1 Introduction

Soil and groundwater contamination by petroleum products is becoming an increasing concern and it is raising an important demand for research, focused on the remediation of the affected media (Bertolla et al. 2014). This contamination is related to different anthropogenic activities, such as accidental spills, leaks from underground storage tanks or pipelines, and/or derived from oil exploitation, smelting, oil transportation, oily wastewater discharge and irrigation (Tang et al. 2012).

In situ chemical oxidation (ISCO) has been widely applied for the remediation of hydrocarbon contaminated soils (Baciocchi 2013; Tsitonaki et al. 2010). Among all ISCO techniques, activated persulfate ($S_2O_8^{2-}$), $E°$= 2.01 V, is becoming an effective alternative to Fenton's reagent, permanganate oxidation or ozonation (Siegrist et al. 2011). Activated persulfate presents a high stability in water and/or soil, it is relatively inexpensive, it produces benign end products and it has a high redox potential of $SO_4^{\cdot-}$ radicals ($E°$=2.60 V), released when PS is activated, and similar to that corresponding to hydroxyl radicals $OH^{\cdot}$=2.70 V (Vicente et al. 2011). All these advantages allow activated-persulfate to oxidize a wide range of contaminants.

To produce $SO_4^{\cdot-}$ radicals, activation of persulfate can be carried out by different ways, such as the addition of a transition metal (Liang et al. 2004a; Zhou et al.

2013; Anipsitakis and Dionysiou 2004); increasing the temperature (Gu et al. 2011; Luo 2014; Tan et al. 2012); the addition of a metal-chelated reagent (Anotai et al. 2011; Liang et al. 2009; Yan and Lo 2013); and pH adjustment, promoting acidic pH (Romero et al. 2010), or alkaline (Liang and Guo 2012; Furman et al. 2010).

When activation is carried out by the addition of Fe(II), the overall reaction is described by Eqs. (1) and (2), which shows resulting an undesired non-productive consumption of PS.

$$S_2O_8{}^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot-} \quad (1)$$

$$SO_4^{\cdot-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \quad (2)$$

In order to solve this disadvantage, the use of ZVI has been proposed in literature, as an alternative to the addition of Fe(II), which has yielded satisfactory results, mainly regarding water treatment (Deng et al. 2014; Liang and Guo 2010; Liang and Lai 2008; Oh et al. 2009) and to a lower extent soil treatment (Oh and Shin 2014).

Despite the benefits of using ZVI as activator, there are some drawbacks that should be taken into account. For instance, the suitability of the injection of ZVI in geological porous media is under discussion because of the difficulties related to the injection of small particles when ZVI is injected in a granular form (millimeters) or powder form (micrometers). Therefore, the use of ZVI in the form of nanoparticles has been proposed as an alternative in order to solve this inconvenience (Al-Shamsi and Thomson 2013).

Furthermore, corrosion of Fe^0 by PS, as described in Eq. (3), leads to the formation of Fe(II). In addition, three further reactions take place in the outer surface of the metallic particles. In this sense, Eq. (4) shows the reduction of Fe(III) to Fe(II) in the presence of ZVI, and both Eqs. (5) and (6) describe the corrosion of the surface (Triszcz et al. 2009).

$$Fe^0 + S_2O_8{}^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \quad (3)$$

$$2\ Fe^{3+} + Fe^0 \rightarrow 3\ Fe^{2+} \quad (4)$$

$$Fe^0 + 2\ H_2O \rightarrow Fe^{2+} + H_2 + 2\ OH^- \quad (5)$$

$$Fe^0 + H_2O + \frac{1}{2}O_2 \rightarrow Fe^{2+} + 2\ OH^- \quad (6)$$

In order to keep iron in solution by minimizing the potential losses related to the solubility limitations of Fe(II) at neutral pH, iron chelate reagents have been studied in the literature. Specifically, the use of either SC or CiA as iron-chelating agents have been studied for the removal of certain pollutants, such as PAHs (Zhao et al. 2013) or herbicides (Vicente et al. 2012) in soils, and aniline (Anotai et al. 2011) or antibiotics (Ji et al. 2014) in water. Few works have used these chelating agents for diesel-contaminated soils. In this sense, the use of sodium citrate has been considered, in previous works, through a Modified Fenton Reagent for the removal of ethylbenzene (Pardo et al. 2014b) and a biodiesel blend (Pardo et al. 2014a), from contaminated soils. Good results were obtained for ethylbenzene (EB) removal while for biodiesel abatement, lower conversions of pollutant were obtained. This can be explained by considering that EB was degraded at a higher rate than the chelating agent. On the contrary, diesel seems to be more recalcitrant to oxidation than SC and CiA, thus chelating agent was faster degraded than this contaminant.

Among all petroleum products, diesel shows a high affinity to soil organic matter in the subsurface media due to its low solubility and low volatility, and this fact makes difficult its abatement from soil and/or groundwater. (Liang and Guo 2012). There are different works in the literature focused on diesel (fossil fuel) removal by using different remediation techniques, such as bioremediation (Chen et al. 2014; Gallego et al. 2001; Marchal et al. 2003; Soliman et al. 2014), AOPs (Tsai and Kao 2009; Villa et al. 2010; Watts and Dilly 1996; Xu et al. 2011) or combination of both AOPs and bioremediation techniques (Pereira et al. 2009; Sutton et al. 2014; Bumbac and Diacu 2012).

In recent years, there has been an increasing interest in the remediation of diesel-contaminated soils, by using PS as oxidant. The main studies are focused on the effect of coupling metal oxides with PS/Fe(II) (Do et al. 2010), the comparison between PS activated by Fe(II) with the most typical oxidants (Yen et al. 2011), the promotion of an alkali media (Liang and Guo 2012); or even the analysis of the application of a ZVI powder (Oh and Shin 2014). On the other hand, some authors have assessed the characteristics of the biota after treatment with PS activated by Fe(II) (Sutton et al. 2014). Little attention has been paid to the change in the diesel fingerprint after the oxidation treatment, and oxidant, iron, and chelating agent profiles during diesel abatement are scarcely studied. Besides, in case of nZVI, there are still no studies which have considered this PS activator for diesel contaminated soils. Moreover, to our

best knowledge, there is not information about the specific removal of biodiesel blends from contaminated media, only limited to groundwater contamination (Mitre et al. 2013).

Therefore, the scope of this work was to assess the effectiveness of persulfate activated by iron (ferrous salt, ZVI and nZVI) or iron chelated (by citric acid or trisodium citrate), for the remediation of a biodiesel blend contaminated soil. The different species involved in the reaction were monitored (TPH removal efficiency, total iron in solution, pH, oxidant and chelating agent concentrations), and the removal of the most representative fractions of the diesel/biodiesel was analyzed.

2 Materials and Methods

2.1 Reagents

Commercial biodiesel/diesel blend was obtained from a road gas station, rest of reagents were analytical grade. Sodium persulfate ≥98 %, as oxidant, was purchased from Sigma-Aldrich. As activators, ferrous sulfate heptahydrate from Fisher Chemical, ferric sulfate from Panreac, gZVI (particle diameter 0.32–0.71 mm) from Aldrich and a slurry of nZVI (NANOFER 25S) by Nanoiron s.r.o., were used. As chelating agents, trisodium citrate 2-hydrate ≥99.0 % (Sigma-Aldrich), and citric acid 99.5 % (Panreac) were added. For PS analysis, sodium hydrogen carbonate 99.7 % (Panreac), potassium iodide >99.5 % (Fisher Chemical), sodium thiosulfate pentahydrate 99.5 % (Sigma-Aldrich), and sodium persulfate ≥98 % (Sigma-Aldrich) were employed.

Nitric acid 69.5 %, provided by Scharlau, was used as iron ions stabilizer in MP-AES analysis. For the analysis of citrate by HPLC, phosphoric acid ≥85 % and potassium phosphate monobasic ≥99.5 %, both purchased from Sigma-Aldrich, were used as mobile phase components. Ultrapure laboratory grade water (MilliQ) obtained from a deionizing system was employed for the preparation of all solutions.

Acetone 99.8 % HPLC gradient grade from Fisher Chemical, n-hexane 99 % HPLC grade from Scharlab and dichloromethane 99.8 % HPLC gradient from Sigma Aldrich, were used in the diesel extraction from soil samples. Sodium sulfate anhydrous 99 %, from Fisher Chemical, was employed for the conditioning of soil reaction samples.

2.2 Diesel Fingerprint Characterization

Taking into account the fingerprint of the fuel used as pollutant, the sum of areas of identified fatty acid methyl esters (FAME), such as hexadecanoic acid (palmitic acid), methyl ester (C17), 8, 11 octadecadienoic acid methyl ester (C19) and 8 octadecenoic acid methyl ester, is about 20 % of the total sum of areas of all compounds (Pardo et al. 2014a). Besides, Fig. 1 shows a representative chromatogram corresponding to a soil sample before being treated.

2.3 Soil Spiking

A sandy clay loam BT horizon from the Autonomous Community of Madrid with neutral pH was selected for this work. The characterization procedure of this soil was described elsewhere (Vicente et al. 2012). The soil contains 0.365 % of soil organic matter (SOM), a pH value of 7.22, and an apparent surface area of 23 $m^2 \cdot g^{-1}$. A more detailed description can be found elsewhere (Pardo et al. 2014b).

The spiking of the soil was carried out by adding 500 mL of a contaminant solution (2 g L^{-1} in n-hexane) on 1 kg of clean soil achieving 1,000 mg kg^{-1} of pollutant in soil. Spiked soil was placed in an orbital shaker for 24 h to ensure homogeneity and after shaking was settled in a fume hood for 48 h to evaporate n-hexane.

2.4 Remediation Runs

Experiments were conducted without pH adjustment, by using 50-mL PTFE centrifuge tubes with PTFE screw caps as batch reactors, stirred isothermally (20 °C) in an orbital shaker (Unitronic Orbital by Selecta) at 100 rpm. Five gram of polluted soil were treated with 10 mL of aqueous solution (V_L/W_S= 2 $mL \cdot g^{-1}$), with the corresponding concentration of the reagents (persulfate, hydrogen peroxide, iron sulfate, trisodium citrate, or citric acid). In case of the experiments with ZVI, it was added (in form of granular particles or slurry of nanoparticles) after the addition of the aqueous solution with the oxidant. Each reaction tube represents one time point. At the selected time, 10 mL of n-hexane/dichloromethane (1:1) were added to the reaction media, and then, the slurry was centrifuged for 10 min at 10,000 rpm

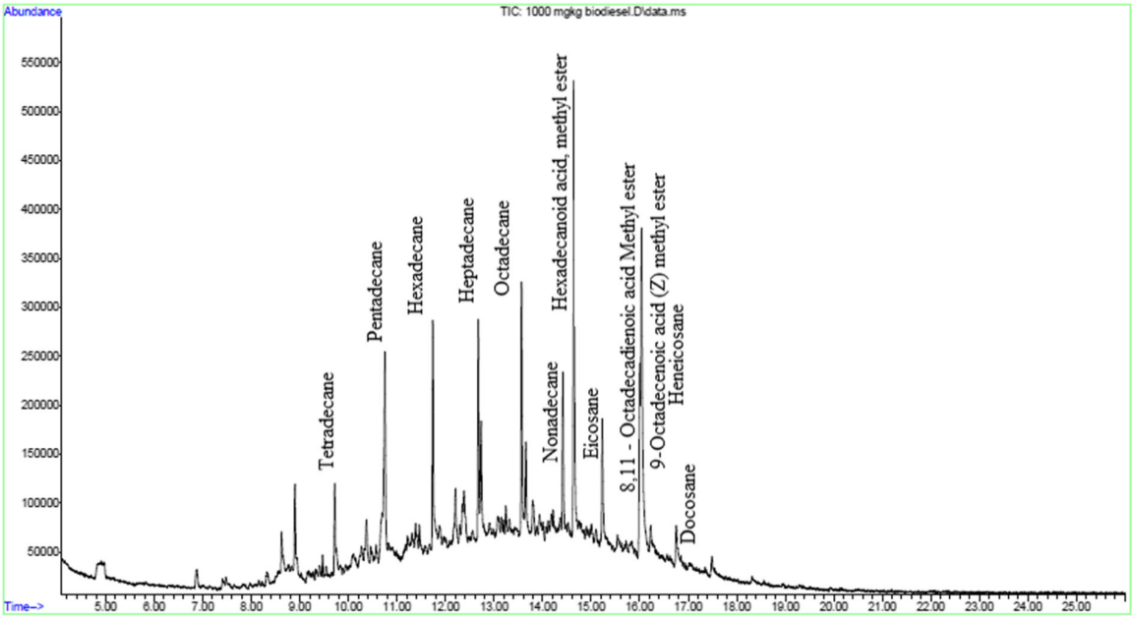

Fig. 1 Representative chromatogram (GC-MS) of a sample of biodiesel-contaminated soil (1,000 mg kg^{-1})

with a Meditronic-BL (Selecta), obtaining three differentiated phases. Organic phase was withdrawn and analyzed by GC-FID; the aqueous supernatant was separated from the soil and then, the pH was evaluated and the remaining Persulfate, H_2O_2, SC, or CiA and total iron concentrations were analyzed. For the analysis of TPH remaining in soil phase after the extraction of the organic phase above mentioned, it has been followed the same procedure reported in a previous work (Pardo et al. 2014a), based on EPA Method 3540C. The experiments carried out are summarized in Table 1.

2.5 Analytical Method

For quantitative analysis of diesel, a GC with flame ionization detection (FID; HP 6890) and equipped with a capillary DB-1 column (30 m×0.25 mm i.d.×1 μm) was used. The diesel concentration was determined by the sum of the total peak area (EPA method 8015B). The chromatographic conditions used were as follows: injector temperature: 280 °C; detector temperature: 330 °C; carrier gas (He) flow rate: 10 mL•min^{-1}. The analysis was performed with an initial oven temperature: 45 °C, followed by a first ramp of 12 °C·min^{-1} to 250 °C and a second ramp of 8 °C·min^{-1} to 325 °C. The final run time was 46.46 min.

Diesel compounds were identified by GC/MS (HP 6890N MSD 5975B), a HP-5 column (30 m×0.32 mm i.d. × 0.25 μm) was used for the analysis. The same chromatographic conditions were used in GC/MS and GC/FID.

For citric acid/citrate determination, a buffer solution with 20 mmol L^{-1} $H_2P_2O_4$, acidified to pH=2.1 with phosphoric acid, was used, and a flow rate of 0.2 mL min^{-1}. The programmed temperature of the column during analysis was 20 °C. A Poroshell 120 SB-C18 in 2.1×100 mm and 2.7 μm of particle size column was used.

The concentration of PS in solution was determined by iodometric titration with a solution of sodium thiosulfate, $Na_2S_2O_3$, of known concentration, by using a potentiometric titration analyzer supplied by Metrohm. pH was measured with a pH glass electrode also supplied by Metrohm.

Analysis of iron was carried out with a microwave plasma-atomic emission spectrometer 4100 MP-AES (Agilent Technologies), a OneNeb nebulizer was used. Sample, previously acidified with 1 % (*v*/*v*) HNO_3, was fed into the MP-AES with a peristaltic pump operating at 8 rpm. The selected wavelength for iron determination was 259.94 nm. Quantification of Fe(II) was made by the method of phenanthroline by using a HACH DR/890 colorimeter.

Table 1 Experimental conditions for runs carried out in batch tests. T=20 °C

Run	PS (mmol L^{-1})	C_{Fe} (mmol L^{-1})	Fe valence	Fe source	Chelating agent (mmol L^{-1})	Chelating agent species	Diesel (mg kg^{-1})	W soil (g)	V liquid (mL)
1	100	0	–	–	0	–	0	5	10
2	200	0	–	–	0	–	0		
3	200	20	III	$Fe_2(SO_4)_3$	50	Sodium Citrate	1,000		
4	200	20	II	$FeSO_4$	50	Citric Acid	1,000		
5	200	20	II	$FeSO_4$	50	Sodium Citrate	1,000		
6	200	20	II	$FeSO_4$	0	–	1,000		
7	200	20	0	Granular ZVI (0.32–0.71 mm ave size)	0	–	1,000		
8	200	20	0	Nano ZVI (50 nm ave size)	0	–	1,000		
9	200	120 (6 doses of nZVI 20 mM)	0	Nano ZVI (50 nm ave size)	0	–	1,000		

3 Results and Discussion

3.1 Non-Productive Consumption of Persulfate

Firstly, the stability of persulfate in contact with this soil has been analyzed (runs 1 and 2). Figure 2 shows the oxidant conversion obtained at the two concentrations used. For the sake of comparison, results obtained for nonproductive consumption of hydrogen peroxide, reported elsewhere (Pardo et al. 2014a), has been also shown in Fig. 2. It is noticed that the consumption of persulfate in a period of 2,000 h (83 days) is very low in this soil, overall compared to that observed for hydrogen peroxide, confirming that stability of persulfate in soil is higher even when it has been added at a concentration 10 times lower than hydrogen peroxide.

3.2 Effect of Chelating Agent Addition

Persulfate activated by chelated iron has been used in literature with a wide variety of contaminants, such as BTEX (Killian et al. 2007), Naphtalene (Yan and Lo 2013), TCE (Liang et al. 2004b), PAH (Lo et al. 2012; Venny et al. 2012; Chang et al. 2013) in soils; or aniline (Anotai et al. 2011) and TCE (Liang et al. 2009) in waters. In this work, the effectiveness of trisodium citrate as chelating agent has been evaluated for the removal of biodiesel. Figure 3 shows the evolution of the different species involved in the reaction, the oxidant (Fig. 3a), chelating agent (Fig. 3b), total iron (Fig. 3c), and pH (Fig. 3d) in the aqueous phase, as well as the removal efficiency of biodiesel measured as TPH in the soil (Fig. 3e). As can be seen, a negligible removal of contaminant was observed after reaction times higher than 100 h, at near-neutral pH or slightly acidic pH, probably due to a poor activation of the oxidant at these experimental conditions, as it can be deduced from the low persulfate and chelating agent conversions. In contrast, the activation of the oxidant at the acidic pH obtained with CiA resulted in a significant consumption of chelating agent, but the removal efficiency of TPH was insignificant. Therefore, the use of both chelating agents was ineffective in the removal with persulfate of the diesel blend. On the other hand, 20 % of removal efficiency was observed after 100 h of reaction and after 20 % of persulfate consumed in the experiment where sodium citrate was not added. This negative effect of

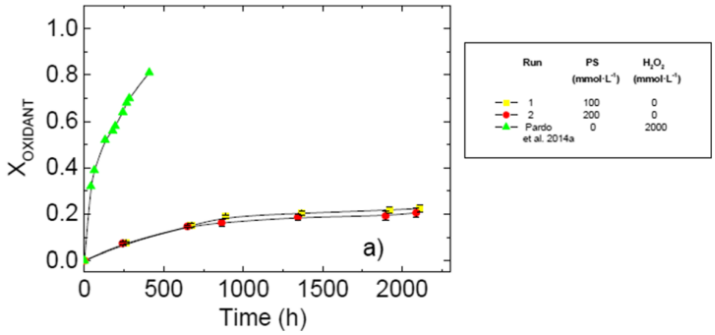

Fig. 2 Consumption of persulfate, in runs 1 and 2, and hydrogen peroxide (Pardo et al. 2014a) as a function of time, at 20 °C, V_L/W_{soil}=2 mL g^{-1}

citrate on the removal rate of a diesel contaminated soil was also noticed elsewhere (Pardo et al. 2014a), by using Modified Fenton Reagent, and can be explained because chelating agent competes with diesel for the oxidant. Diesel is more recalcitrant to oxidation than the chelating agents here used and therefore the chelating agent was ineffective in diesel abatement.

3.3 Influence of Types of Iron on the Activation of Persulfate

The activation of persulfate has been carried out by using three different forms of iron, such as Fe(II) from ferrous iron ($FeSO_4$), gZVI and nZVI. The evolution of the different species involved in the reaction, when 200 mmol·L^{-1} persulfate and 20 mmol·L^{-1} iron

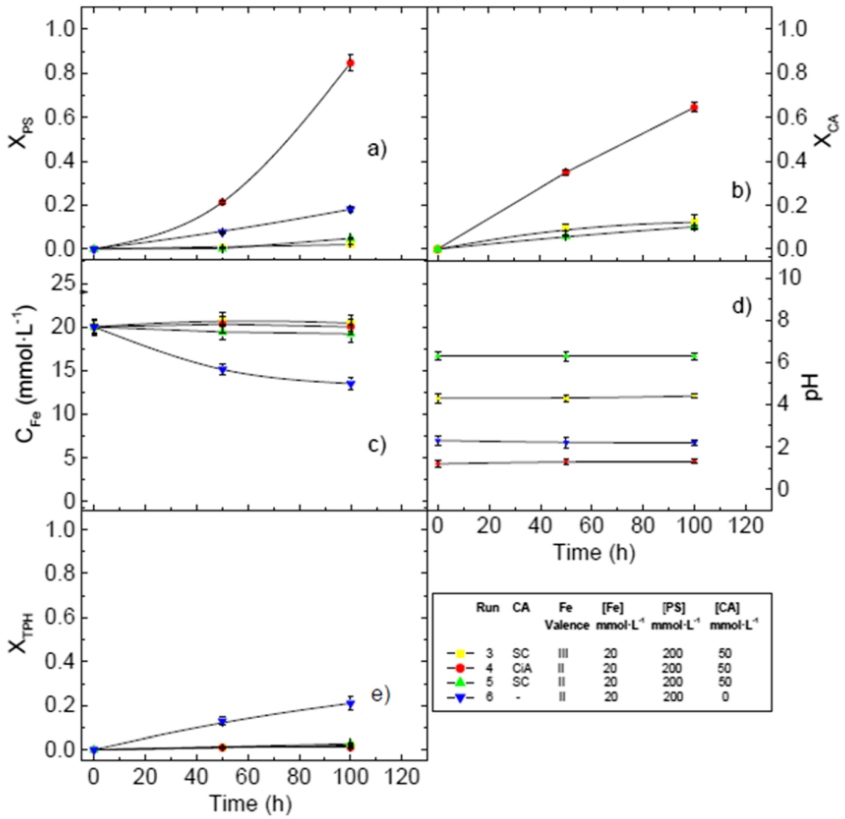

Fig. 3 Evolution of the reaction media on the removal of TPH with persulfate, SC and CiA as chelating agents, at different pH: (*a*) X_{PS} vs t; (*b*) X_{CA} vs t; (*c*) C_{Fe} vs t; (*d*) pH vs t; (*e*) X_{TPH} vs t and at 20 °C, V_L/W_{soil}=2 mL g^{-1}

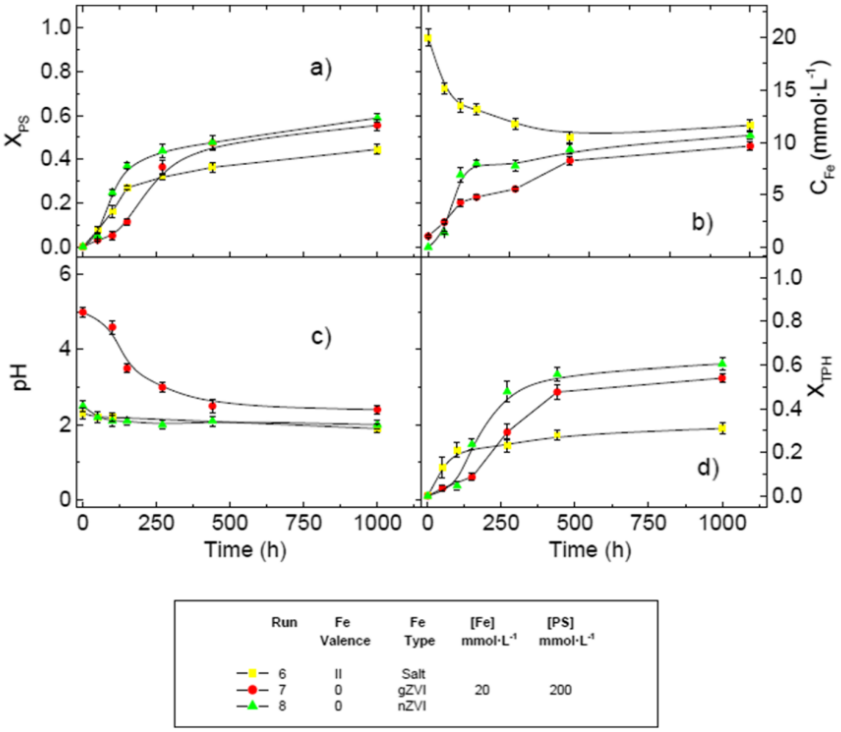

Fig. 4 Evolution of the reaction media, influence of iron source: (*a*) X_{PS} vs t; (*b*) C_{Fe} vs t; (*c*) pH vs t; and (*d*) X_{TPH} vs t, at 20 °C, V_L/W_{soil}=2 mL g^{-1}

concentration, for the ferrous salt, was studied. The same iron amount added in run 6 as Fe(II) was employed in runs 7 and 8 as gZVI and nZVI, respectively. The reaction time was extended to 1,000 h in run 6, as well as for run 7 (gZVI) and 8 (nZVI). Figure 4 collects the persulfate conversion (Fig. 4a), total iron in solution (Fig. 4b), pH (Fig. 4c), and biodiesel removal efficiency (Fig. 4d).

A plateau in PS conversion after 500 h of reaction (20 days) can be observed in Fig. 4a, obtaining only slightly higher consumptions of PS at 1,000 h when ZVI was used, either in form of gZVI or nZVI. These results can be explained by the fact that two molecules of PS are necessary to produce a $SO_4^{\cdot-}$ radical (Eqs. (1) and (3)) when ZVI is used, due to ZVI corrosion by PS. However, only a molecule of PS is necessary for the production of a $SO_4^{\cdot-}$ radical (Eq. (1)), in case of Fe(II) activation.

With regard to total iron in solution, it can be seen in Fig. 4b that the iron concentration in solution tends to a value around 10 mmol·L^{-1}, for the three runs 6 to 8, in accordance with solubility of iron (III) in solution, at a pH close to 2 (Martí 2002). In the case of ZVI (granular and nanoparticles), the concentration profile is very different and the total iron in solution is increasing progressively along the reaction, working as a

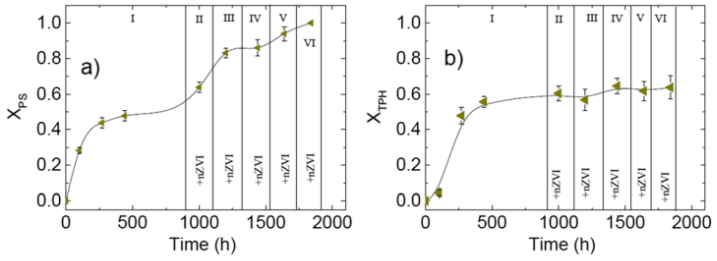

Fig. 5 Evolution of oxidant and TPH removal efficiency, additional doses of nZVI: (*a*) X_{PS} vs t; (*b*) C_{TPH} vs t; [PS]=200 mmol L^{-1}, [Fe_{nVZI}] =20 mmol L^{-1}, at 20 °C, V_L/W_{soil}=2 mL g^{-1}

Table 2 Most representative compounds in the biodiesel sample analyzed

Compound	Number of carbons	$\frac{A_{Identified}}{\sum A_{Identified}} \times 100$
Aliphatic compounds		
Tetradecane (TD)	14	4.58
Pentadecane (PD)	15	6.60
Hexadecane (HXD)	16	11.94
Heptadecane (HPD)	17	13.20
Octadecane (OD)	18	11.79
Nonadecane (ND)	19	4.67
Eicosane (EC)	20	3.88
Heneicosane (HEC)	21	3.68
Docosane (DOC)	22	3.55
FAME		
Hexadecanoic acid methyl ester (HDME)	17	12.77
8,11-Octadecadienoic acid methyl ester (OME1)	19	23.33
9-Octadecenoic acid (Z) methyl ester (OME2)	19	

continuous releasing source of iron ions for PS activation (Rodriguez et al. 2014). However, with Fe(II) activation, an earlier decrease in iron in solution was observed, associated to the quicker oxidation of Fe(II) to Fe(III) and its, consequently, precipitation.

Figure 4d shows the removal efficiency of TPH as a function of the reaction time. As can be seen, TPH removal efficiency was higher for PS activated with nanoparticles (about 60 % at 1,000 h reaction), followed by gZVI (54 %). Nevertheless, Fe(II) activation showed a removal efficiency of 31 %. In this sense, some authors reported that PS activation by Fe(II) can be hindered due to sulfate radical scavenging by excess of Fe(II), and this fact results in a loss of sulfate radicals for the abatement of the pollutant (Liang et al. 2004a, 2007; Rodriguez et al. 2014; Vicente et al. 2011). Furthermore, due to the fact that ZVI works as a continuous releasing source of Fe (II), minimizing the unproductive reaction in Eq. (2), better results were obtained compared to that in which Fe(II) was added once (Deng et al. 2014; Oh et al. 2009). Therefore, the addition of ZVI is more efficient than the use of the same concentration of Fe(II).

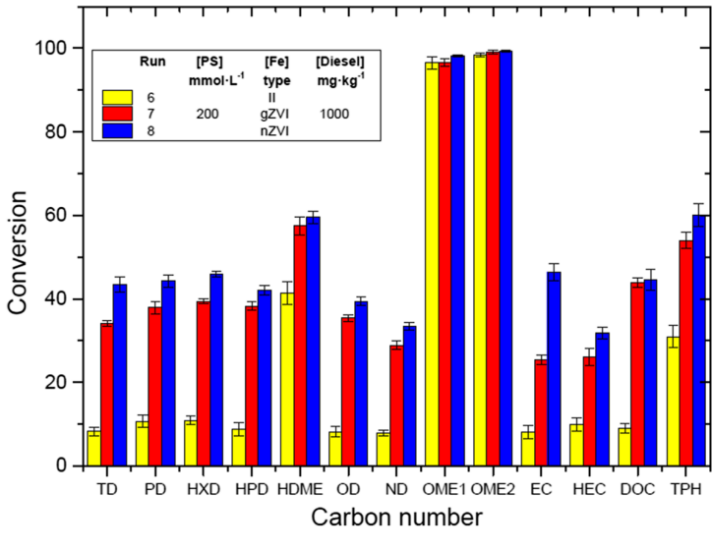

Fig. 6 Conversion of the different diesel fractions, from C14 to C22, influence of iron source. T=20 °C, V_L/W_{soil}=2 mL g^{-1}

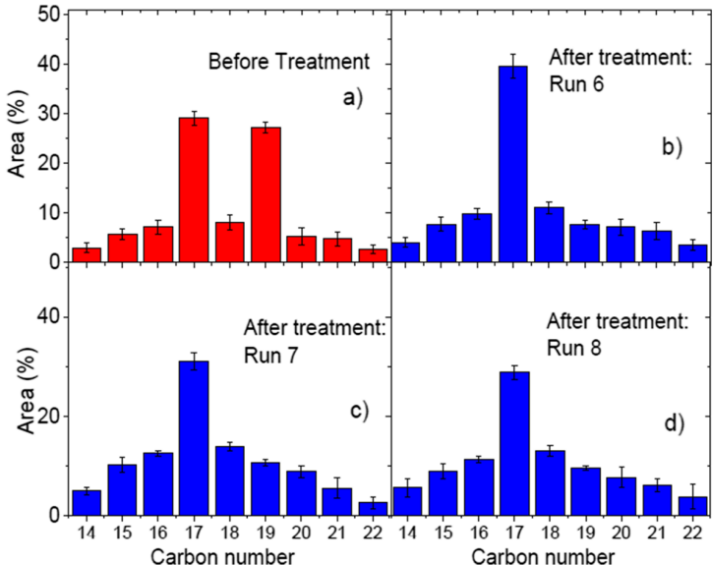

Fig. 7 Fingerprints of diesel (C14–C22) before and after the treatment with persulfate activated by different sources of iron

3.4 Influence of Sequential Doses of Iron Nanoparticles

After 1,000-h reaction, a total consumption of PS was not achieved, and there were still a significant biodiesel remaining in the soil. Therefore, run 9 consisted on the repetition of run 8 until 1,000 h, followed by five consecutive additions of nZVI 20 mM onto the soil in order to verify the extent of biodiesel removal. These additional doses were added every 240 h until total consumption of persulfate. Figure 5 shows the conversions of persulfate and TPH as a function of the reaction time, during the additional dosage of ZVI, respectively. As can be seen in Fig. 5a, total consumption of PS was achieved after the fifth further addition of iron. In contrast, only a slight improvement in biodiesel removal was also noticed, see Fig. 5b. Although nanoparticles improve TPH removal efficiency, there is a fraction of pollutant that remains in the soil which is more difficult to oxidize. In this sense, different authors have reported different TPH removal efficiencies at various soil characteristics and reagents doses, but to our best knowledge, there is not reported total contaminant destruction, but TPH conversion was usually in the range of 40–60 % in soil contaminated by diesel (Do et al. 2010; Liang and Guo 2012; Yen et al. 2011).

Table 3 Removal efficiency of aliphatic and FAME identified compounds, respectively, in runs 6–8

Run	$X_{\text{Aliphatic}}$	X_{FAME}
6	0.09	0.78
7	0.34	0.84
8	0.39	0.85

3.5 Removal of the Different Fractions of Biodiesel Identified

Up to now, the results only show, in general, the conversion of TPH. However, for the sake of analyzing which kinds of fractions are more affected by the treatment with persulfate, the most representative components found in this diesel fingerprint have been analyzed. Table 2 summarizes these most representative components found in this biodiesel, but only considering a range of number of carbons between 14 and 22. Last column in Table 2 correspond to the ratio between the area of a specific compound to the sum of areas of all identified compounds.

Figure 6 shows the corresponding conversion of the different fractions of biodiesel in the experiments, at 1,000 h, with activated persulfate by Fe(II), gZVI and nZVI, respectively (runs 6–8). As can be seen, the most relevant result is the pronounced decreasing in FAME abatement, mostly for the C19 FAMEs (OME1 and OME2) and for the C17 (HDME). Another important aspect to point out is the similar conversion values found when persulfate is activated by gZVI and nZVI. However, the conversions, when Fe(II) is used, are

considerably lower, excepting for the C19 and C17 compounds, which present very similar values. It is also important to mention the improvement on the removal of the more recalcitrant fractions (aliphatic hydrocarbons) with the use of ZVI. These results could be associated to the lowest availability of the sulfate radicals for the abatement of the pollutant due to scavenging reactions. This low availability may produce that only the most reactive fraction reacts, explaining the poor performance with the most stable compounds.

The distribution of the different identified fractions in the contaminated soil before and after the treatment, classified by the number of carbons, is shown in Fig. 7. Taking into account that oxidation of C19 FAME compounds where near 100 %, changes in the distribution of compounds show that C17 compounds are the main fraction of the remaining biodiesel, corresponding to the presence of HD and HDME. The rest of the compounds present a very similar distribution after the treatment, pointing out a slight relative percentage of the aliphatic fractions after the treatment.

Finally, Table 3 shows the comparison of FAME and Aliphatic identified compounds conversions at different experimental conditions, those corresponding to the higher removal efficiencies obtained, (Fe(II) (run 6), gZVI (run 7) and nZVI (run 8) activated persulfate). As can be seen in Table 3, lower removal efficiencies were obtained for aliphatic compounds. These results are expectable, due to the well-known lower reactivity to oxidation of these compounds with regard to that of FAME.

4 Conclusions

The study of the remediation of a biodiesel blend-contaminated soil by iron-activated persulfate was carried out by analyzing the influence of the activator source and the effect of the chelating agent in the efficiency of the remediation. PS was found to be much more stable in soil than hydrogen peroxide, showing a much lower unproductive consumption. Both chelating agents used, trisodium citrate and citric acid, were ineffective in diesel abatement, because of the neutral pH promoted by SC and the competition of CiA for the sulfate radicals. Diesel was more recalcitrant to oxidation than aromatic compounds as those studied elsewhere (Pardo et al. 2014a).

The TPH removal obtained by using different source of activator followed the increasing sequence, activation with Fe(II) (31 %), gZVI (54 %) or nZVI (60 %). Furthermore, the reaction with nZVI was extended with additional doses of activator and it was observed that TPH removal was not improved significantly with the consecutive additions, probably due to oxidation resistance of aliphatic hydrocarbons.

The results indicated that soil remediation with persulfate activated with nZVI is a promising technique, due to the stability of the oxidant in soil and the advantages of injecting in field a slurry of nZVI instead of granular metallic particles. However, a deeper study would be necessary, for nZVI activation, to optimize the process (dosages and times).

Acknowledgments The authors acknowledge financial support from the Comunidad Autonoma de Madrid provided throughout project CARESOIL (S2009AMB-1648) and from Spanish Ministry of Science and Innovation, project CTM2010-16693.

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4.3 Eliminación de hidrocarburos aromáticos policíclicos (PAHs)

El último tipo de contaminante que se seleccionó para la presente tesis fueron los hidrocarburos aromáticos policíclicos, que como ya se indicó en la introducción, su eliminación de focos contaminados (aguas subterráneas, suelos, etc.) es de carácter prioritario en el ámbito de la recuperación de suelos, dado el potencial carcinogénico y mutagénico de algunos de los componentes, además de su persistencia en suelo (alta hidrofobicidad, baja volatilidad y baja solubilidad en agua). Dada la enorme variedad de hidrocarburos aromáticos policíclicos, se han identificado más de 100 tipos diferentes (desde el más simple, naftaleno, con 2 anillos aromáticos, hasta el coroneno, con 7 anillos). Se seleccionaron antraceno y fenantreno como componentes representativos de PAHs de 3 anillos, pireno con 4 anillos y benzo(a)pireno con 5 anillos. Los tratamientos llevados a cabo fueron, en el siguiente orden, reactivo Fenton en discontinuo, persulfato activado en discontinuo y persulfato activado en columna.

4.3.1 Reactivo Fenton (Artículo 4)

Durante el tratamiento de suelo contaminado con etilbenceno aplicando el reactivo Fenton modificado se obtuvieron resultados de conversión casi completa del contaminante. Sin embargo, al cambiar etilbenceno por biodiesel B20 como contaminante, se observó que el agente quelante se oxidaba más rápidamente que incluso en el tratamiento con etilbenceno, obteniéndose bajas eficiencias de eliminación (X_{TPH} máximo = 37%). El biodiesel se elimina en un mayor grado cuando el reactivo Fenton se utiliza sin adición de agente quelante; sin embargo, el consumo de oxidante fue demasiado rápido, lo que la convertía en una alternativa poco práctica de cara a aplicarla en suelos reales.

Por tanto, para la eliminación de PAH se buscaron alternativas a las que se probaron con respecto al reactivo Fenton. Para evitar un consumo excesivo de oxidante en tiempos cortos, se trabajó sobre un rango de concentraciones de hierro inferior a los anteriormente utilizados, siendo para este estudio de C_{Fe0} = 1 – 5 mmol·L^{-1}. Además, se probó la adición de catalizador en forma de nZVI y Fe(III) como sulfato férrico. Por último, se estudió la combinación de oxidación química con uso de surfactantes, utilizando en este caso SDS como agente tensoactivo.

Antes de los tratamientos se comprobó el consumo improductivo de peróxido además de la eliminación de contaminantes para un blanco (adición de agua Milli-Q sobre el suelo contaminado) y un lavado con surfactante (C_{SDS0} = 7.6 mmol·L^{-1}). Tras 40 días se comprobó una eficiencia de eliminación de los contaminantes del suelo entre un 15-20%. En la tabla 4.4 se muestran las conversiones finales de cada uno de los contaminantes con cada uno de los tratamientos.

Influencia de la concentración de hierro

El estudio del efecto de la concentración de hierro se realizó manteniendo fija la concentración inicial de H_2O_2 (882 mmol·L^{-1}) y modificando la concentración inicial de hierro (0 - 1 – 5 mmol·L^{-1}). Los resultados mostrados en el artículo ponen de manifiesto que cuando se añadió el Fe(III) a la máxima concentración (5 mmol·L^{-1}) se observan unas conversiones prácticamente totales de los contaminantes (X_{PAH} > 99%) y que las reacciones transcurren al pH más ácido y el consumo de oxidante alcanzó la totalidad en aproximadamente 10 días.

Al añadir hierro a una concentración inicial de 1 mmol·L^{-1} se consiguió eliminar antraceno y benzo(a)pireno totalmente, pero a una velocidad inferior a la obtenida cuando la concentración inicial de Fe fue de 5 mmol·L^{-1}. Las mayores diferencias se observaron con respecto a fenantreno y pireno, ya que las conversiones pasaron de ser completas con $C_{Fe(III)0}$ = 5 mmol·L^{-1} a ser de un 79% con $C_{Fe(III)0}$ = 1 mmol·L^{-1} y 66% con $C_{Fe(III)0}$ = 0 mmol·L^{-1} para fenantreno y de un 44% con $C_{Fe(III)0}$ = 1 mmol·L^{-1} y 34% con $C_{Fe(III)0}$ = 0 mmol·L^{-1} para pireno.

La disminución de la dosis de hierro también se tradujo en un pH menos acido del medio de reacción y un consumo de oxidante más lento hasta su completa degradación. Cuando no se añadió hierro al medio, tanto el hierro disuelto como el pH del medio fueron prácticamente idénticos, sin embargo las conversiones de contaminantes que se alcanzaron fueron algo inferiores, este hecho podría venir explicado por la formación y precipitación de los hidróxidos de hierro a partir del sulfato de hierro al encontrarse a un pH demasiado elevado.

Influencia del tipo de hierro

En este caso se comparó entre el uso de Fe(III) y hierro cerovalente como catalizadores del peróxido de hidrógeno, a una concentración inicial de hierro de 1 $mmol \cdot L^{-1}$, observándose un mayor rendimiento en la eliminación de los contaminantes cuando se añadió Fe(III). Aunque las concentraciones de hierro en disolución acuosa medidas fueron similares en ambos casos, el pH al que transcurrieron las reacciones con nanopartículas fue menos ácido, lo que limitó la solubilidad del hierro en agua y, en consecuencia la eficiencia de eliminación de los contaminantes.

Influencia de la concentración de oxidante

El estudio de la concentración de oxidante se llevó a cabo añadiendo el catalizador en forma de Fe(III) como sal de sulfato férrico a una concentración inicial de Fe(III) de 1 $mmol \cdot L^{-1}$, y modificando la concentración inicial de H_2O_2 ($C_{H_2O_20}$ = 882 $mmol \cdot L^{-1}$ y 1765 $mmol \cdot L^{-1}$). Se observó que los perfiles de antraceno y fenantreno fueron bastante similares, alcanzándose prácticamente la misma conversión de contaminante. Para el caso del pireno la conversión fue mayor (67% con $C_{H_2O_20}$ = 1765 $mmol \cdot L^{-1}$ y 44% con $C_{H_2O_20}$ = 882 $mmol \cdot L^{-1}$) y el benzo(a)pireno llegó a conversión completa en menos tiempo.

En consecuencia, a pesar de haber incrementado la concentración inicial de oxidante al doble, la mejora en las eficiencias de eliminación de los contaminantes no fue tan significativa. Este fenómeno normalmente se da cuando el propio exceso de oxidante ejerce un papel de secuestro de radicales hidroxilo, HOO (Ec. [4.10]), formándose el radical perhidroxilo, de menor potencial oxidante (1.7 V) que el propio radical hidroxilo (2.8), resultando en una sensible mejora en la eliminación de los contaminantes (Romero et al., 2009)

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HOO^{\cdot} \qquad k = 2.7 \cdot 10^{-7}\ (M^{-1} \cdot s^{-1}) \qquad [4.10]$$

Lavado y oxidación química

Los experimentos en los que se probó el efecto del surfactante sobre el proceso de oxidación química fueron realizados bajo las siguientes condiciones iniciales, $C_{H_2O_20}$ = 882 $mmol \cdot L^{-1}$ y $C_{Fe(III)0}$ = 1 $mmol \cdot L^{-1}$. El surfactante, dodecil sulfato de sodio,

biodegradable y no tóxico (cita), fue añadido a su concentración micelar crítica (C_{SDS0} = 7.6 mmol·L^{-1}).

Además se estudió el efecto del surfactante añadiéndolo al mismo tiempo que el oxidante y el catalizador, y añadiéndolo 24 horas antes, con objeto de incrementar la disponibilidad de los contaminantes, que el oxidante y el catalizador. A la vista de los resultados, la acción del surfactante permitió mejorar las conversiones de pireno y fenantreno, mientras que para antraceno y benzo(a)pireno se alcanzó conversión completa.

También se observó que tras iniciar el proceso de oxidación 24 h después de añadir el surfactante se alcanzaron las mismas eficiencias de eliminación que cuando se añadieron todos los reactivos al mismo tiempo, aunque se requirió menos tiempo para alcanzar dichas conversiones.

Por último, es preciso destacar que el subproducto de oxidación de estos contaminantes mayoritario que fue detectado fue 9-10, antraquinona.

4.3.2 Persufato activado (Artículo 5)

Después de probar la eliminación de hidrocarburos con reactivo Fenton, se utilizó persulfato activado con diferentes fuentes de hierro (Fe(II), Fe(III) y nZVI). Además, se probó el efecto, por separado, de la incorporación de ácidos húmicos y surfactante en el medio de reacción. En todos los tratamientos realizados, se estudió la influencia del tipo de hierro como activador (tipos), del efecto de la adición de surfactante y ácidos húmicos así como del efecto de la concentración de las nZVI.

A partir de los resultados obtenidos, se desarrollaron modelos cinéticos para describir el consumo de oxidante y de contaminantes con el tiempo. Los tratamientos se llevaron a cabo durante 50 días y durante ese tiempo se siguió la evolución de los distintos contaminantes, expresada como conversiones, el pH del medio de reacción y la concentración de oxidante.

Influencia del tipo de hierro

Los experimentos se llevaron a cabo a 20ºC, sin ajuste previo del pH, manteniendo fija la concentración inicial de persulfato C_{PS0} = 200 mmol·L^{-1} y la

concentración inicial de hierro, que independientemente del tipo de activador añadido fue de 1 $mmol \cdot L^{-1}$. Las reacciones transcurrieron a un pH que fue decreciendo de ligeramente ácido (en torno a 5) a ácido (cerca de 2).

De los resultados relacionados con las conversiones de los contaminantes a lo largo del tiempo se observó que tanto antraceno como benzo(a)pireno se eliminaron casi totalmente (99%), al igual que sucedió durante los tratamientos con reactivo Fenton, en los cuatro primeros días de reacción. Las especies más resistentes volvieron a ser fenantreno y pireno. Los mejores resultados correspondieron a la activación con nZVI, lo mismo que sucedió cuando el contaminante fue biodiesel B20.

Influencia del surfactante y ácidos húmicos

Este estudio se realizó manteniendo fija la concentración inicial de persulfato (200 $mmol \cdot L^{-1}$) y de hierro (1 $mmol \cdot L^{-1}$). En primer lugar se estudió el efecto de ambas variables sobre la aplicación de persulfato activado por Fe(II), y por nZVI por otro. En el artículo 5 se muestran únicamente las conversiones de fenantreno y pireno, ya que en todos los casos se consiguieron eficiencias de eliminación completas tanto de antraceno como de benzo(a)pireno.

Con la adición del surfactante SDS se consiguieron mejorar sensiblemente las eficiencias de eliminación de fenantreno y pireno, mientras que la adición de ácidos húmicos no supuso una mejora significativa en los tratamientos.

Influencia de la concentración de hierro

En cuanto a la concentración de hierro, principalmente el aumento, de 1 $mmol \cdot L^{-1}$ a 5 $mmol \cdot L^{-1}$ se tradujo en un mayor incremento en el consumo de persulfato que de conversión de los contaminantes.

Modelo cinético

Para la determinación del modelo cinético que permitiese describir la evolución de los contaminantes y del agente oxidante con el tiempo se partió de una cinética de pseudo orden 1, que como ya aparece indicado en literatura (Siegrist et al., 2011), es la más frecuente para este tipo de tratamientos por oxidación química in situ, ya que el

agente oxidante se suele añadir en un exceso importante respecto del estequiométrico, y su variación a lo largo del tiempo no es tan significativa como la variación de la concentración de PAH, para conseguir vencer el consumo improductivo por especies presentes capaces de reaccionar con el agente oxidante.

Las ecuaciones 4.11 a 4.16 describen el tratamiento matemático utilizado para describir la evolución de la conversión del contaminante X_{PAHj} con el tiempo, (Ec. [3.16]). k es la constante cinética intrínseca ($L \cdot dia^{-1} \cdot mmol_{PS}^{-1}$), C_{PS} la concentración de persulfato ($mmol \cdot L^{-1}$) en la fase acuosa, C_{PAHj} la concentración de cada PAH (ANT, PHE, PYR y BaP) en el suelo ($mg \cdot kg^{-1}$), k_{obs} (dia^{-1}) es la constante cinética observada, como resultado del producto entre k y C_{PS}.

$$\frac{-dC_{PAH_j}}{dt} = k \cdot C_{PS} \cdot C_{PAH_j} \quad [4.11]$$

$$k_{obs} = k \cdot C_{PS} \quad [4.12]$$

$$\frac{-dC_{PAH_j}}{dt} = k_{obs} \cdot C_{PAH_j} \quad [4.13]$$

$$C_{PAH_j} = C_{PAH_{jo}} \cdot e^{-k_{obs} \cdot t} \quad [4.14]$$

$$X_{PAHj} = \frac{C_{PAH_{jo}} - C_{PAH_j}}{C_{PAH_{jo}}} \quad [4.15]$$

$$X_{PAHj} = 1 - e^{-k_j \cdot t} \quad [4.16]$$

La conversión de persulfato, asumiendo que la contribución de los PAH en su consumo no era significativa (baja solubilidad en agua y baja concentración), está determinada principalmente por su consumo improductivo (k_{unp}) y por la presencia de hierro (k_{PSFe}) y está descrita en la Ec. [4.17]:

$$X_{PS} = 1 - e^{-(k_{unp} + k_{PSFe}) \cdot t} \quad [4.17]$$

4.3.3 Persufato activado en columna (Artículo 6)

Una vez establecidos los correspondiente modelos cinéticos (artículo 5), se realizaron una serie de ensayos de remediación en columna con objeto de estudiar la

eficiencia del tratamiento con persulfato activado tras añadir Fe(III) y nanopartículas de hierro cerovalente.

Durante los 25 días que duraron los tratamientos se monitorizaron las variables más importantes del proceso a la salida de la columna, pH, concentración de persulfato y concentración de hierro en disolución.

Al finalizar los 25 días de experimento, se estudiaron las conversiones de los contaminantes y el perfil de hierro lábil a lo largo de la columna y se compararon los resultados con los estimados, simulando el comportamiento de la columna con los modelos obtenidos del anterior estudio en los que se utilizó Fe(III) como activador.

Influencia del tipo de hierro

Para comparar el tipo de hierro como activador, se utilizó la misma concentración de persulfato a la entrada de la columna (C_{PS0} = 200 mmol·L^{-1}) y se introdujeron cantidades similares de hierro. Se alimentó Fe(III), a una concentración de 1 mmol·L^{-1}, en forma de sulfato férrico y se inyectó simultáneamente con el persulfato, durante los 25 días que duró el tratamiento. Por otro lado, se inyectó una suspensión con nZVI (1 mmol·L^{-1} en hierro) durante 25 días, creando una zona de activación dentro del suelo para la posterior inyección del persulfato durante otros 25 días. Bajo estas condiciones, las mejores eficiencias de eliminación se consiguieron cuando la activación se realizó con nZVI que con Fe(III).

Los perfiles a lo largo de la columna, tanto de hierro, analizado e identificado como hierro lábil, como de concentración de contaminantes, mostraron ligeras diferencias entre ambos tipos de activación. Aunque los perfiles hallados tras la activación con Fe(III) fueron más pronunciados que con nZVI, ambos presentaron la misma tendencia, localizándose una mayor concentración de hierro lábil a la entrada de la columna y una mayor conversión de los contaminantes, estando estos dos factores estrechamente relacionados.

De las conversiones de contaminantes se observaron tendencias muy similares a las observadas en el artículo 5, donde benzo(a)pireno y antraceno se oxidaban más fácilmente que pireno y fenantreno, el contaminante más resistente. Sin embargo, a diferencia del anterior trabajo, en el suelo que se utilizó n la columna fue sometido a un

breve proceso de envejecimiento de tres meses, se observó degradación natural de antraceno a antraquinona. Este subproducto de oxidación mostró una mayor resistencia a la oxidación que los contaminantes de partida.

Influencia de la concentración de hierro

Se evaluó también la eficiencia de eliminación de los contaminantes incrementando considerablemente la dosis de hierro a la entrada, con una suspensión de nZVI a una concentración de 900 mmol·L^{-1}. Sin embargo, esta suspensión solamente fue alimentada a la columna durante un día, comenzándose a inyectar el persulfato al segundo día. Tras el tratamiento de 25 días se observaron perfiles menos pronunciados que en los casos anteriores tanto de hierro como de conversión de los contaminantes a lo largo de la columna. Además, el aumento en la dosis de hierro a la entrada resultó en una ligera mejora en las eficiencias de eliminación de los contaminantes.

Estimación modelo cinético

En base a los modelos cinéticos obtenidos del artículo 5, se utilizó aquel en el que se añadió Fe(III) 1 mmol·L^{-1} como activador para estimar las concentraciones, y por tanto las conversiones de contaminantes a la salida de la columna (Ec. [4.18]), y de persulfato (Ec. [4.19]). Donde k_w es la constante observada (aparente) (dia^{-1}), k_{wPS} es la constante para el consumo de persulfato, ρ_L es la densidad del lecho de suelo (1.445 g·cm^{-3}), L es la longitud del lecho (17.5 cm) y u_i es la velocidad lineal del fluido a lo largo de la columna (cm·dia^{-1}). Los resultados obtenidos mostraron un buen ajuste del modelo con respecto a las conversiones alcanzadas como promedio de toda la columna, pero divergiendo considerablemente en los extremos, es decir, tanto a la entrada como a la salida.

$$1 - X_{PAH_j} = e^{-k_{w_j} \cdot t} \qquad [4.18]$$

$$C_{PS} = C_{PS_0} \cdot e^{-k_{wPS} \cdot \rho_L \cdot L} / u_i \qquad [4.19]$$

Tabla. 4.4. Resumen de las eficiencias de eliminación para cada uno de los diferentes tratamientos llevados a cabo en la aplicación del reactivo Fenton para la eliminación de PAH (ANT, PHE, PYR y BaP). Tª = 20 ºC, sin ajuste previo del pH del medio. C_{PAHjo} = 100 mg·kg^{-1}, W_S = 5 g, V_L = 10 mL, V_L/W_S= mL·g^{-1}. Tiempo final de tratamiento: 40 días.

C_{H2O20}		*Fuente hierro*	C_{Fe0}		C_{SDS0}		X_{PAH}^{final}			
mmol·L^{-1}	*mg·L^{-1}*		*mmol·L^{-1}*	*mg·L^{-1}*	*mmol·L^{-1}*	*mg·L^{-1}*	*ANT*	*PHE*	*PYR*	*BaP*
882	30000	$Fe_2(SO_4)_3$ Fe(III)	1	55.8	-	-	>99%	79%	44%	>95%
882	30000	$Fe_2(SO_4)_3$ Fe(III)	5	280	-	-	>99%	>99%	>99%	>99%
882	30000	-	-	-	-	-	>99%	66%	34%	>99%
882	30000	Nanopartículas hierro cerovalente	1	55.8	-	-	>99%	45%	36%	>99%
882	30000	Nanopartículas hierro cerovalente	5	280	-	-	79.8%	45%	40%	80%
1765	60000	$Fe_2(SO_4)_3$ Fe(III)	1	55.8	-	-	>99%	82%	67%	>99%
882	30000	$Fe_2(SO_4)_3$ Fe(III)	1	55.8	7.6	2200	>99%	75%	81%	>99%
882 (24h)	30000	$Fe_2(SO_4)_3$ Fe(III)	1 (24h)	55.8	7.6	2200	>99%	79%	86%	>99%

Tabla. 4.5. Resumen de las eficiencias de eliminación para cada uno de los diferentes tratamientos llevados a cabo en la aplicación de persulfato acivado para la eliminación de PAH (ANT, PHE, PYR y BaP). T^a = 20 ºC, sin ajuste previo del pH del medio. C_{PAHjo} = 100 mg·kg^{-1}, C_{PS0} = 200 mmol·L^{-1}, W_S = 5 g, V_L = 10 mL, V_L/W_S = 2 mL·g^{-1}. Tiempo final de tratamiento: 50 dias.

Fuente hierro	***C_{Fe0}***		***C_{SDS0}***		***Ácidos Húmicos***	***X_{PAH}^{final}***			
	mmol·L^{-1}	***mg·L^{-1}***	***mmol·L^{-1}***	***mg·L^{-1}***	***mg·L^{-1}***	***ANT***	***PHE***	***PYR***	***BaP***
$FeSO_4$ Fe(II)	1	55.8	-	-	-	>99%	57%	>99%	>99%
$Fe_2(SO_4)_3$ Fe(III)	1	55.8	-	-	-	>99%	48%	93%	>99%
Nanopartículas hierro cerovalente	1	55.8	-	-	-	>99%	86%	>99%	>99%
$FeSO_4$ Fe(II)	1	55.8	7.6	2200	-	>99%	62%	95%	>99%
Nanopartículas hierro cerovalente	1	55.8	7.6	2200	-	>99%	96%	94%	>99%
$FeSO_4$ Fe(II)	1	55.8	-	-	2000	>99%	52%	91%	>99%
Nanopartículas hierro cerovalente	5	280	-	-	-	>99%	90%	93%	>99%

Tabla. 4.6. Resumen de las eficiencias de eliminación para cada uno de los diferentes tratamientos llevados a cabo en la aplicación de persulfato acivado para la eliminación de PAH (ANT, PHE, PYR y BaP). T^a = 20 ºC, sin ajuste previo del pH del medio. C_{PAHjo} = 100 mg·kg^{-1}, C_{PS0} = 200 mmol·L^{-1}, Q_0 = 43.2 cm^3·dia^{-1}, u = 13.9 cm·dia^{-1}. Tiempo de tratamiento : 25 días.

Fuente hierro	***C_{Fe0}***		***Zona***	***X_{PAH}^{final}***				
	mmol·L^{-1}	***mg·L^{-1}***		***ANT***	***ATQ***	***PHE***	***PYR***	***BaP***
-	-	-	**I**	-	-	-	-	-
			II	-	-	-	-	-
			III	-	-	-	-	-
			IV	-	-	-	-	-
			Media	>99%	7%	7%	56%	96%
$Fe_2(SO_4)_3$ Fe(III)	1	55.8	**I**	>99%	34%	91%	93%	>99%
			II	>99%	18%	60%	90%	>99%
			III	>99%	14%	24%	87%	>99%
			IV	>99%	10%	12%	77%	>99%
			Media	>99%	19%	46%	87%	>99%
Nanopartículas hierro cerovalente	1	55.8	**I**	>99%	36%	90%	93%	>99%
			II	>99%	20%	67%	92%	>99%
			III	>99%	18%	48%	91%	>99%
			IV	>99%	11%	33%	88%	>99%
			Media	>99%	21%	58%	91%	>99%
	900	50000	**I**	>99%	40%	90%	95%	>99%
			II	>99%	29%	81%	95%	>99%
			III	>99%	30%	78%	95%	>99%
			IV	>99%	23%	75%	94%	>99%
			Media	>99%	30%	81%	95%	>99%

ARTÍCULO 4/ ARTICLE 4

Título/*Title*: Optimization of the application of the Fenton chemistry for the remediation of a contaminated soil with polycyclic aromatic hydrocarbons.

Autores/*Authors*: Fernando Pardo, Marina Peluffo, Aurora Santos, Arturo Romero.

Estado actual/*current status*: Journal of Chemical Technology and Biotechnology. Junio/*June* 2016, 91:6, 1763 – 1772.
Recibido/*Received*: 24-04-2015. Revisado/Revised: 22-06-2015. Aceptado para publicación/*Accepted for publication*: 26-06-2015. Publicado Online/*First Published online*: 17-07-2015.

DOI: 10.1002/jctb.4767

Factor de impacto/Impact factor (JCR, 2014): 2.349

Research Article

SCI

Received: 24 April 2015 Revised: 22 June 2015 Accepted article published: 26 June 2015 Published online in Wiley Online Library:

(wileyonlinelibrary.com) DOI 10.1002/jctb.4767

Optimization of the application of the Fenton chemistry for the remediation of a contaminated soil with polycyclic aromatic hydrocarbons

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Abstract

BACKGROUND: A contaminated soil with 100 mg kg^{-1} each of the following pollutants: anthracene (ANT), phenanthrene (PHE), pyrene (PYR) and benzo(a)pyrene (BaP) was treated by three different kinds of Fenton's reaction without pH adjustment, Fenton-like reaction (hydrogen peroxide (H_2O_2) with a ferric iron salt (Fe(III)), Fenton catalyzed with nanoparticles of zerovalent iron (nZVI), and Fenton-like reaction coupled simultaneously with soil washing, using sodium dodecyl sulfate (SDS) as surfactant.

The influence of initial iron concentration (1–5 mmol L^{-1}), oxidant dosage (88–1765 mmol L^{-1}), type of iron initially added (Fe(III) or nZVI) and effect of surfactant addition were tested.

RESULTS: Almost total conversion of ANT and BaP was achieved for the majority of the experiments, having obtained the best results for the Fenton like reaction with initial Fe(III) concentration of 5 mmol L^{-1}, where a total abatement for all contaminants was obtained in less than 10 days. Besides, the coupling of Fenton reagent and soil washing enhanced the removal of the PAHs studied. 9–10 anthraquinone (ATQ) was detected as the main aromatic intermediate.

CONCLUSIONS: The results put forward in this work reveal the suitability of new effective alternatives to conventional Fenton Reagent for the removal of PAH in soils.

Keywords: : PAHs; Fenton's Reagent; zerovalent iron nanoparticles; surfactant

INTRODUCTION

The presence of polycyclic aromatic hydrocarbons (PAHs) in soils may be due to natural phenomena (e.g. forest fires) or, to a greater extent, anthropogenic activities (incomplete combustion of wood, fuel, coal, etc.). As a consequence, PAHs are usually found at important concentrations, in hazardous waste sites such as manufactured gas plants, coal coking plants, etc.[1,2] Despite their low solubility in water, the presence of PAHs in subsoil is frequent; as they can interact with soil organic matter (SOM) they can also reach the water table in the form of non-aqueous phase liquids (NAPLs), such as creosote, coal tar or diesel fuel.[3,4]

Due to their toxicity and carcinogenic potential, the need for controlling the pathways from the sources of contamination to human exposure (e.g. inhalation, skin contact or ingestion of soil particles) has become of increasing concern.[5,6] This increasing concern has resulted in the development of a large number of technologies for the removal of this kind of pollutant in the last two decades, such as solvent extraction, which includes soil washing with surfactants, organic solvents, cyclodextrins, subcritical and supercritical fluids; anaerobic or aerobic bioremediation; phytoremediation; photocatalytic and electrokinetic remediation; chemical oxidation using Fenton's reagent, ozone, persulfate, permanganate, etc.; integrated treatments such as biological–chemical, physical–chemical or physical–chemical–biological.[7,8]

Among chemical oxidation processes, also called advanced oxidation processes (AOPs), special attention has been paid to the use of Fenton's reagent, which consists in the release of hydroxyl radicals, with high oxidation potential ($E° = 2.73$ V), from the catalytic decomposition of H_2O_2 by Fe(II) or Fe(III), having the ability to oxidize a wide range of organic pollutants. However, implementation of this technique has to deal with important factors which affect critically the efficiency of the process. First, with respect to the oxidant, hydroxyl radical's lifetime is short and there is also a non-productive consumption of H_2O_2, due to its interaction with SOM and iron, manganese oxyhydroxides

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or other transition metals in solution;[9,10] regarding catalyst, iron cation precipitates at circumneutral pH, resulting in important problems of loss of catalyst;[11,12] and finally, regarding the organic nature of the contaminant, its low solubility in water hinders the mass transfer between phases. In order to solve these aforementioned drawbacks, the oxidant doses onto the soil must be added at higher quantities to ensure a total degradation of the contaminants,[13,14] pH of the reaction must be kept at acidic conditions, or a chelating agent can be added in order to keep iron in solution at near neutral pH,[8,15,16] and a surfactant can be added simultaneously to the oxidant in order to increase contaminant solubility in the aqueous phase.[17,18]

As reported elsewhere,[15] the chelating agent (CA) competes with the contaminant for the oxidant, and consequently, the oxidant concentration available for the pollutant decreases. Moreover, if pollutants are more recalcitrant to oxidation than the chelating agent, the contaminant removal efficiencies can diminish owing to the CA.

The catalyst added in Fenton's reagent has usually been an iron salt (Fe(II) or Fe(III)), but in recent years, zerovalent iron (ZVI) has been also tested, mainly in aqueous phase.[19,20] In the case of Fenton's reagent applied to remediation of contaminated soils, nanoparticles of zerovalent iron (nZVI) could be injected into the subsurface as a continuous source of iron. The use of nZVI in soil remediation has been described in the literature as a method of chemical reduction for some contaminants,[21] but little attention has been paid to the use of nZVI as a source of iron in soil remediation by Fenton's reagent.

Besides, until this moment, the coupling of soil washing and chemical oxidation in soil remediation, also called surfactant enhanced chemical oxidation (SCO), has been scarcely studied in soil remediation.[17,18] However, it could be a potential combined method for the abatement of pollutants with high hydrophobicity (as PAHs) while the surfactant promotes the solubilization of these compounds to the aqueous phase and the oxidation reaction takes place in this same phase.

Therefore, the aim of this work is to study the remediation of a contaminated soil by 4 PAH, (PHE), (ANT), (PYR) and (BaP), all included in the 16 PAHs priority list of the EPA, by using Fenton's reagent under different conditions, catalyzed by Fe(III), nZVI and using a surfactant coupled to the Fenton's reagent. Oxidant, total iron in solution, contaminant conversion and pH were followed during the reaction, and the effects of oxidant concentration, iron concentration, source of iron and surfactant addition were studied. Besides, aromatic intermediates were identified and quantified in order to evaluate the effectiveness of each technique, not only in terms of removal efficiency of the contaminants.

EXPERIMENTAL

Reagents

PHE ≥ 96% (HPLC grade) from Sigma, ANT 99% from Aldrich, PYR 98% from Aldrich and BaP ≥96% from Aldrich were used as contaminants and for the preparation of calibration levels for their analysis by HPLC. For the remediation runs, H_2O_2 ≥ 35% (RT) from Sigma-Aldrich was used as oxidant; ferric sulfate from Panreac 75% (anhydrous basis) and air-stable nZVI powder (NANOFER STAR) from Nanoiron s.r.o. were used, respectively, as catalyst species. For soil washing and coupled soil washing with Fenton reagent, SDS ≥99%, from Sigma-Aldrich, was used as surfactant. For H_2O_2 determination, sulfuric acid >95%, from Fisher Chemical, and potassium permanganate 99.5%, from Panreac, were both used. Sodium sulfate anhydrous 99%, from Fisher Chemical, acetone 99.8% HPLC gradient grade from Fisher Chemical and n-hexane 99% HPLC grade from Scharlab were used for extraction of the contaminant in the soil samples. Dichloromethane ≥99.8% HPLC grade from Sigma-Aldrich was used for the analysis of intermediates. Phosphoric acid ≥85% from Sigma-Aldrich and Acetonitrile HPLC gradient grade from Fisher Chemical were both used as mobile phase in HPLC for PAH analysis. For metal determination in aqueous solution in MP-AES analysis, nitric acid 69.5% was employed as iron ions stabilizer.

Table 1. Concentration of each contaminant in the spiked soil

	Number of rings	Concentration (mg kg^{-1})
ANT	3	97 ± 6
PHE	3	89 ± 2
PYR	4	93 ± 1
BaP	5	102 ± 1

Soil spiking

The soil used for the remediation runs consists of a sandy clay loam BT horizon from the Autonomous Community of Madrid; the characterization procedure and a detailed description of the properties are given elsewhere.[22,23] Soil spiking was carried out as detailed in the literature,[24,25] where an acetone solution with approximately 60 mg of each ANT, PHE, PYR and BaP was distributed and mixed manually onto 600 g of clean soil with a spatula. Table 1 shows the concentrations achieved for each recovered PAH in soil, after soxhlet extraction.

Set-up and procedure

All experiments were carried out without pH adjustment in batch mode using 50 mL PTFE centrifuge tubes with PTFE screw caps. An orbital shaker (Unitronic Orbital by Selecta), under isothermal stirring (100 rpm, 20 °C) was used and tubes were placed horizontally in the shaker. Each reaction tube represents one time point, in which 10 mL of aqueous solution (V_L) were added to 5 g of polluted soil (W_{soil}). Two tubes for each time were used in order to get duplicated values. As can be seen in Table 2, five different types of runs were conducted: non-productive consumption of oxidant (NPC) to study the interaction of the non-polluted soil with the oxidant; a blank run (BL) without addition of oxidant in the aqueous phase; a soil washing (SW) run using an aqueous solution of SDS 7.6 mmol L^{-1}; runs using Fenton's Reagent without surfactant (FR runs), or with surfactant (SCO runs). With regard to the experiments which involved surfactant addition (SW or SCO), SDS was added at its critical micelle concentration (CMC), 7.6 mmol L^{-1} (20 °C).[26,27] Initial iron concentration $[Fe]_o$, type of iron (ferric sulfate or nZVI) and initial oxidant concentration $[H_2O_2]_o$ were the variables modified in the FR runs. In SCO runs the influence of adding the surfactant previously or simultaneously to the oxidant was also analyzed.

In runs where H_2O_2 was added, a control tube was used only for determination of the remaining oxidant every 24–48 h throughout the reaction time. Afterwards, having achieved specified oxidant conversions (about 25, 50, 75 and 100%), two centrifuge tubes with the same reaction time, were sacrificed (measurements were obtained by duplicate and differences were lower than 15%). After centrifugation for 10 min at 10 000 rpm, two differentiated

Table 2. List of experiments performed $V_L = 10$ mL. $V_L/W_S = 2$ mL g^{-1}, $T = 20$ °C

	Run	Fe type	$[Fe]_o$ mmol L^{-1}	$[H_2O_2]_o$ mmol L^{-1}	Polluted soil	$[SDS]_0$ mmol L^{-1}
NPC	1	-	-	882	No	-
BL	2	-	-	-	Yes	-
SW	3	-	-	-		7.6
FR	4	III	1	882		-
FR	5	III	5	882		-
FR	6	-	-	882		-
FR	7	nZVI	1	882		-
FR	8	nVZI	5	882		-
FR	9	III	1	1765		-
SCO	10	III	1	882		7.6
SCO	11	III	1 (24 h)	882 (24 h)		7.6

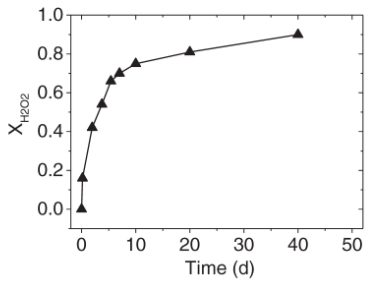

Figure 1. Non-productive consumption of H_2O_2. at 20 °C, $V_L/W_{soil} = 2$ mL g^{-1}, $[H_2O_2]_0 = 882$ mmol L^{-1}.

phases were obtained. 50 µL of the aqueous phase were taken for quantification of the remaining H_2O_2, 500 µL of aqueous phase were filtered (≤45 µm) for the analysis of iron in solution, and a glass pH electrode was inserted in the aqueous phase for pH measurement. Subsequently, the aqueous phase was extracted with 10 mL n-hexane, and after filtration (≤45 µm) of the organic extract, 1 mL was taken for PAH analysis by HPLC.

Remaining PAHs in the soil phase were extracted by Soxhlet extraction, following the method described by the EPA (method 3540 C). About 5 g of soil were extracted using a mixture of n-hexane–acetone (50:50 v:v), as reported in previous work.[15] PAHs were identified in the organic phase after extraction using HPLC. For the identification of possible reaction intermediates, about 20 mL of the organic phase, after extraction, were evaporated at room temperature in a fume hood and reconstituted in 2 mL dichloromethane by GC/MS.

Analytical method

H_2O_2 concentration was measured by potentiometric titration with potassium permanganate 0.005 mol L^{-1} under acidic conditions (sulfuric acid 10%). For the analysis of iron, 20 mL of ultrapure water, previously acidified with HNO_3, with final concentration of 1% v/v in acid, were added to 500 µL of the filtrated aqueous phase from the slurry. This solution was fed into a microwave plasma-atomic emission spectrometer 4100 MP-AES (Agilent Technologies) with a peristaltic pump operating at 8 rpm. The selected wavelength for iron determination was 259.94 nm and a OneNeb nebulizer was used.

The presence of reaction intermediates was analyzed by GC/MS (HP 6890 N MSD 5975B).A HP-5 column (30 m × 0.32 mmol L^{-1} i.d. × 0.25 µm) was used for the analysis. The chromatographic conditions were as listed: injector temperature 280 °C; carrier gas (He) flow rate 2 mL min^{-1} and 8 µL of injected volume in splitless mode. The analysis was performed with an initial oven temperature 45 °C, followed by a first ramp of 5 °C min^{-1} to 150 °C and a second ramp of 8 °C min^{-1} to 325 °C. The final run time was 62.88 min.

For original PAH determination, an HPLC (Agilent, mod. 1100) coupled with an Agilent 1290 Infinity Diode Array Detector was employed. The column used was a Poroshell 120 SB-C18 in 2.1 mm × 100 mm and 2.7 µm particle size. Analysis was carried out in isocratic mode at a flow rate of 0.5 mL min^{-1}, selecting as mobile phase a mixture of 60% acetonitrile and 40% aqueous solution with phosphoric acid 75 mmol L^{-1}; the volume injected was 20 µL. The wavelengths chosen for each PAH were 235 nm for PYR, 250 nm for PHE, and 295 nm for ANT and BaP. The corresponding detection limits for PAHs were 0.27 mg L^{-1} for PHE, 0.11 mg L^{-1} for ANT, 0.37 mg L^{-1} for PYR and 0.47 mg L^{-1} for BaP.

RESULTS AND DISCUSSION

Non-productive consumption of hydrogen peroxide

First, the non-productive consumption of oxidant in soil was studied by following its conversion – Equation (1) – over 20 days of reaction (H_2O_2 882 mmol L^{-1}). Oxidant conversion has been calculated as:

$$X_{H_2O_2} = \frac{C_0^{H_2O_2} - C_t^{H_2O_2}}{C_0^{H_2O_2}} \quad (1)$$

where C_0 *is* the initial concentration of H_2O_2 and C_t is the concentration at a given time. The evolution of oxidant (H_2O_2 882 mmol L^{-1}) with time in run 1 (NPC), within 40 days, is shown in Fig. 1. As can be seen in Fig.1, the oxidant is decomposed unproductively by reacting with the soil organic matter, and catalytically by the soil metal oxides, such as Fe or Mn, which may interact with H_2O_2, leading to the Fenton-like reaction.[28] Therefore, an oxidant amount higher than that, calculated by stoichiometry for the pollutant amount in soil, should be added.[14] Fastest consumption of the oxidant is noticed in the first 10 days before it was slowed down. This decrease may occur due to a first faster stage of soil organic matter and reduced species oxidation and a second catalytic stage, in which the oxidant is still interacting with metal oxides from soil.[10,29] As can be seen, about 80% of the initial oxidant was consumed in the 20 days.

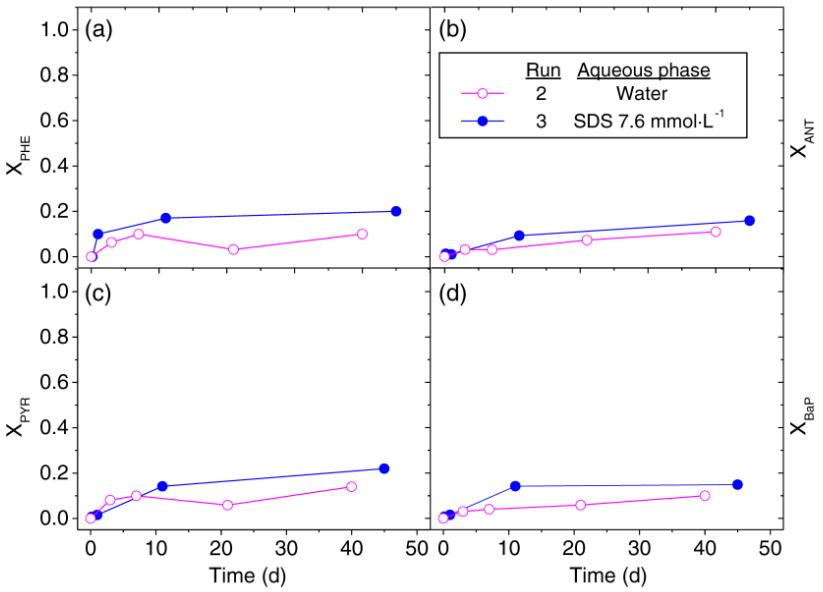

Figure 2. Preliminary runs (blank and soil washing). Evolution of the conversion of PHE, ANT, PYR and BaP in soil. Runs at 20 °C, $V_L/W_{soil} = 2$ mL g^{-1}.

Soil washing and blank experiments

Before the remediation experiments, two runs were performed by adding, on one side, ultra-pure water (BL, run 2), and on the other, a surfactant solution of SDS 7.6 mmol L^{-1} on the contaminated soil (SW, run 3). Concentration of each pollutant was monitored with time in order to evaluate the possibility of biodegradation[25,30] and the effectiveness of soil washing alone. The contaminant conversion – Equation (2) – has been calculated for each PAH:

$$X_{PAH} = \frac{C_0^{PAHj} - C_t^{PAHj}}{C_0^{PAH}j} \qquad (2)$$

with C_0^{PAH} the initial concentration of the *j* PAH (*j* = PHE, ANT, PYR, BaP) in soil and C_t^{PAH} the concentration of the PAH in soil at time *t*. In SW and BL runs, given that leaking to the aqueous phase was negligible for BL run (<1%) and a little bit higher for the SW run (~5%), PAH conversion corresponds to the PAH degraded by natural attenuation during this period. Evolution of the conversion of each PAH in BL and SW runs is shown in Fig. 2. The PAH conversion showed a similar trend for all PAHs. As can be seen in Fig. 2, after 45 days, a plateau at about 15–20% conversion was achieved for all contaminants, both in control and soil washing runs. Moreover, a slightly higher PAH conversion was observed for SW run, which could be explained by the fact that surfactants improve biological degradation of organic contaminants given their ability to improve their solubility through micelle formation and also their mobility due to the decrease of interfacial tension.[31,32]

Taking into account the low organic matter content in the soil treated (0.3%), its ability to develop some kind of biodegradation, without additional stimulation is very limited due to the lack of nutrients for microorganisms.[33,34]

Influence of iron concentration

For the study of the influence of iron concentration on the application of Fenton's Reagent, ferric sulphate was added, without pH adjustment, at two different concentrations, Fe(III) 1 mmol L^{-1} and Fe(III) 5 mmol L^{-1}, both compared with a run in which no iron was added (FR, runs 4, 5 and 6).

Figure 3 shows the evolution of oxidant conversion (3(a)), pH (3(b)), and iron in solution (3(c)), as well as the corresponding conversions of each PAH, PHE (3(d)), ANT (3(e)), PYR (3(f)) and BaP (3(g)).

When aqueous and soil phase were separated and extracted, as well as in the blank and soil washing runs, no significant concentrations of PAHs were detected from the organic extract of the aqueous phase (<1% with respect to the soil organic extract) in any of the runs using Fenton's Reagent.

From Fig. 3(a) to 3(c), a faster consumption of oxidant was observed for the run where initial concentration of Fe(III) was 5 mmol L^{-1}. Given that ferric sulfate is an acidic salt, the addition of ferric sulfate resulted in a decrease of the pH of the media. Besides, as can be seen in Fig. 3(c), a significant amount of the iron initially added precipitated in a short time. Moreover, the results obtained without external addition of iron are similar to those obtained by adding initially 1 mmol L^{-1} Fe(III). This can be explained by taking into account that iron can be extracted from that naturally occurring in soil, in fact, concentration of iron in solution after adding 1 mmol L^{-1} of Fe(III) and iron extracted from soil are quite similar, with the Fenton-like reaction taking place where hydrogen peroxide is catalyzed by the metals present in soil.[28,35]

Knowing that the maximum rate of hydroxyl radical in the catalytic cycle – Equations (3) and (4) – is at about pH = 3,[12,36,37] the faster consumption of H_2O_2 when 5 mmol L^{-1} of Fe(III) is added can be attributed to a higher iron concentration in solution and lower pH of the reaction media.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH\cdot + OH^- \qquad k = 63\ L\ mol^{-1}\ s^{-1} \qquad (3)$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2\cdot + H^+ \qquad k = 0.01\ L\ mol^{-1}\ s^{-1} \qquad (4)$$

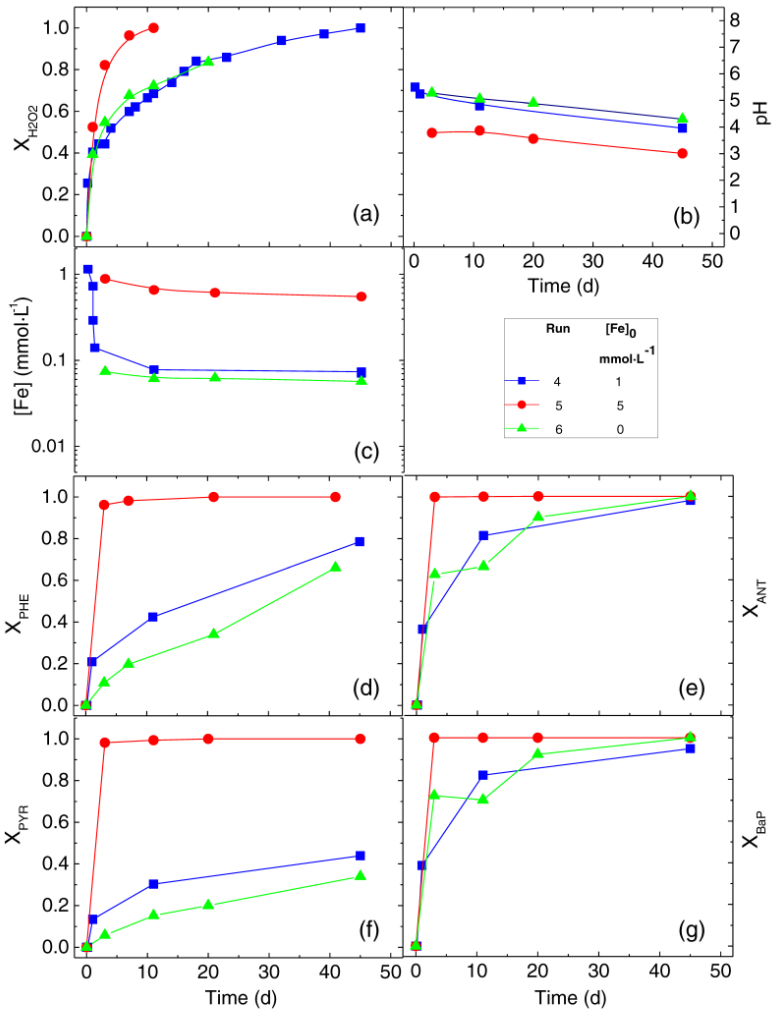

Figure 3. Influence of initial Fe(III) concentration. Evolution of H_2O_2 conversion (a), pH (b), iron in solution (c). PAHs conversion, PHE (d), ANT (e), PYR (f), and BaP (g). at 20 °C, $V_L/W_{soil} = 2$ mL g^{-1}, $[H2O]_0 = 882$ mmol L^{-1}.

With respect to the PAH removal efficiencies (Fig. 3(d) to 3(g)), the best results were observed when Fe(III) 5 mmol L^{-1} was added. Similar results were observed in cases where Fe(III) initial concentration was 1 mmol L^{-1} or when no iron was added, as aforementioned, the close values of iron in solution found, the reaction occurred at almost identical conditions in both runs. In the case of adding Fe(III) 5 mmol L^{-1}, the higher the Fe concentration in solution (about 1 mmol L^{-1}) the higher the amount of hydroxyl radicals released into the media – Equations (3) and (4) – yielding higher conversion of each of the PAHs, achieving almost total abatement of the pollutants in less than 5 days. However, for runs 5 and 6, where iron remaining in solution is as low as 0.1 mmol L^{-1}, significant removal efficiencies were also achieved, almost 100% for ANT and BaP, near 80% for PHE and 40% for PYR.

Influence of the type of iron added (ferric sulfate or nZVI)

To study the influence of different sources of iron on the effectiveness of the Fenton reaction, iron was added as a ferric salt (FR, runs 4 and 5) or as nZVI (FR, runs 7 and 8). Runs 4 and 7 had an initial iron concentration in the aqueous phase of 1 mmol L^{-1}, while in runs 5 and 8 initial iron concentration was 5 mmol L^{-1}.

Figure 4 shows the evolution of the H_2O_2 conversion (4a), pH (4b) and iron concentration in solution (4c) with time. As can be seen in Fig. 4(a) to 4(c), no significant differences in oxidant consumption and pH were noticed with reaction time in runs 4 and 7 ($[Fe]_0 = 1$ mmol L^{-1}). Besides, no differences were found between adding nZVI at 1 mmol L^{-1} (run 7) or 5 mmol L^{-1} (run 8). These similar values obtained in runs 4, 7 and 8 can be explained by the low and almost constant iron in solution observed in these runs. Regarding total iron concentration in solution in Fig. 4(c), a sharp decrease is seen at the beginning in run 4, while in runs 7 and 8 concentration remains constant over time. The fast initial drop of iron noticed after the addition of the iron salt can be explained by both the iron solubility with pH and the iron–soil interaction that enhances iron precipitation or adsorption onto the soil;[38] on the other hand, in runs 7 and 8, iron was added in the form of metallic

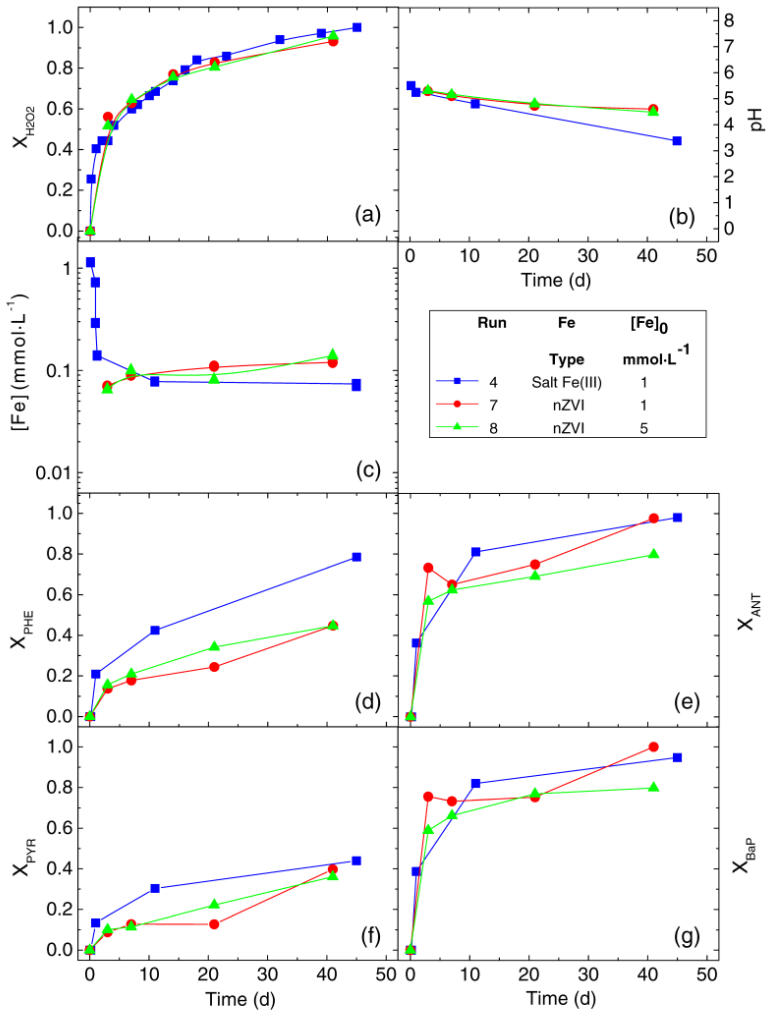

Figure 4. Influence of iron valence initially added. Evolution of H_2O_2 conversion (a), pH (b), iron in solution (c). PAHs conversion, PHE (d), ANT (e), PYR (f), and BaP (g). at 20 °C, $V_L/W_{soil} = 2$ mL g^{-1}, $[H2O]_0 = 882$ mmol L^{-1}.

nZVI and the iron measured was iron in solution, which was also affected by iron solubility with pH and interaction between nZVI and soil.

On the other hand, results in Fig. 4(d) to 4(g) show the removal efficiency of the PAHs. As can be seen, similar results were obtained in runs 4, 7 and 8, as expected from the iron in solution found in Fig. 4(c). As reported in the literature, H_2O_2 catalyzed by nZVI has been successfully employed for the removal of several pollutants, in which better results were obtained when pH was adjusted to 3.[39,40] The negligible improvement noticed in this work by using nZVI could be attributed to the higher pH here used, which limits the iron solubility. However, the nZVI could be an efficient method for the injection of iron into the subsurface, as it can be distributed and act as a continuous source of iron.

Influence of H_2O_2 concentration

Two experiments were carried out in order to analyze the influence of H_2O_2 concentration. For this purpose, initial H_2O_2 concentrations were fixed at 882 mmol L^{-1} or 1765 mmol L^{-1} in runs 4 and 9, respectively. In the case of the addition of H_2O_2 882 mmol L^{-1}, the oxidant/contaminant molar ratio was 15 times higher than stoichiometric (for the sum of PAHs), while for H_2O_2 1765 mmol L^{-1} this concentration was near 30 times higher. The Fe(III) concentration initially added was 1 mmol L^{-1} in both cases.

Figure 5 shows the evolution of H_2O_2 consumption (a), pH (b) and total iron (c) concentration with time. Slightly faster oxidant conversion is observed at lower H_2O_2 concentration. On the other hand, pH and Fe in solution have very similar profiles during the reaction. The first stage of H_2O_2 consumption corresponds to the SOM and reduced species in the soil, while the second is a catalytic stage due to the metal oxides in the soil, therefore it is expected that the higher the H_2O_2 amount in the media, the slower its conversion in the first stage, when the rest of the variables remain fixed.[14]

According to Fig. 5(d) to Fig. 5(g), where conversions of each PAH are shown, an improvement in the removal rate of PYR and BaP

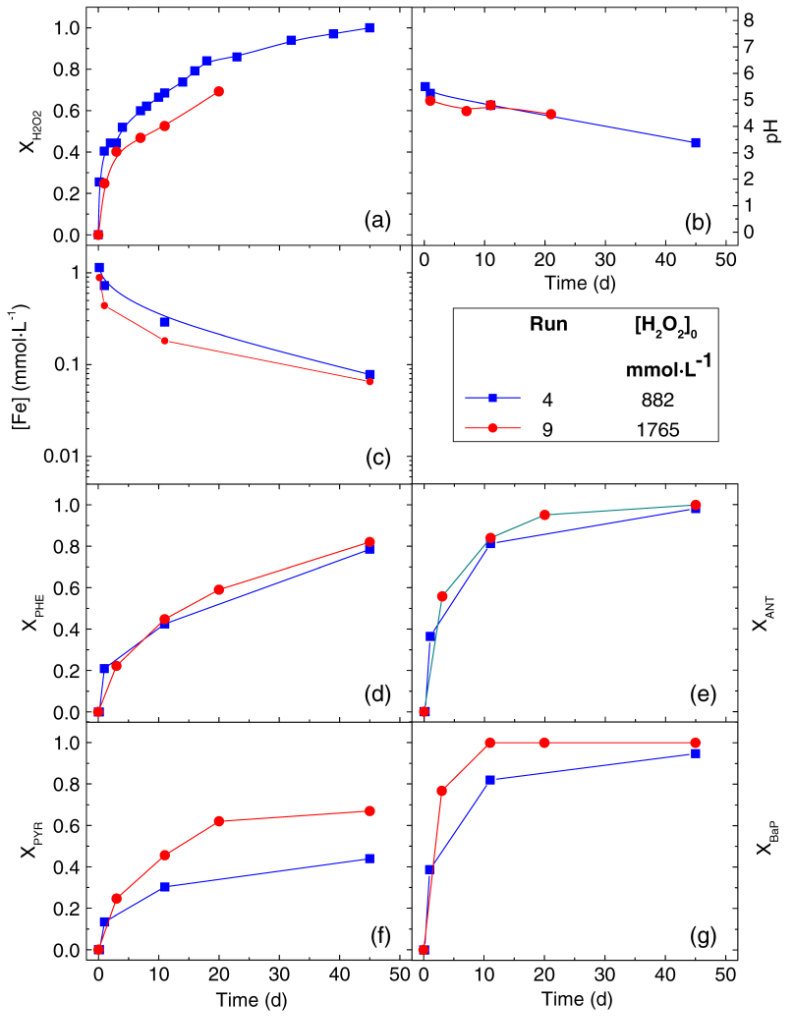

Figure 5. Influence of H_2O_2 concentration. Evolution of H_2O_2 conversion (a), pH (b), iron in solution (c). PAHs conversion, PHE (d), ANT (e), PYR (f), and BaP (g). at 20 °C, $V_L/W_{soil} = 2$ mL g^{-1}, $[Fe]_0 = 1$ mmol L^{-1} added as Fe(III) salt.

was seen while no significant differences were observed for ANT and PHE removal rates. As can be seen, although concentration was increased two-fold, PAHs removal efficiency was increased to a smaller extent, explained by the scavenging effects on hydroxyl radicals due to an excess of H_2O_2.

Application of soil washing and chemical oxidation simultaneously

In order to analyze the possibility of enhancement in the remediation effectiveness, by simultaneous application of a surfactant (SDS) and Fenton's Reagent, results obtained in runs 4, 10 and 11 were compared. Iron was initially added as a ferric salt at a 1 mmol L^{-1} Fe (III) concentration and initial H_2O_2 concentration was fixed at 882 mmol L^{-1}. In run 10, SDS was added simultaneously with the oxidant while in run 11 oxidant and iron were added 24 h after surfactant addition. In run 4 no SDS was added.

Figure 6 shows the evolution of H_2O_2 consumption (a), pH (b) and total iron (c) in solution during the reaction. According to graphs 6(a), 6(b) and 6(c), no remarkable differences in the results for H_2O_2 consumption and Fe in solution (runs 4, 10 and 11), were noticed; in fact, profiles of H_2O_2 conversion and Fe evolution both follow an almost identical trend. In the case of pH, a higher pH was observed for the experiment where SDS was added 24 h prior to the addition of oxidant and iron.

According to Fig. 6(d) to (f), where the conversion of every PAH is shown, PHE (d), ANT (e), PYR (f) and BaP (g), the addition of SDS (runs 10 and 11) resulted in faster abatement of all the PAHs studied. Total conversion was obtained for ANT and BaP while conversions obtained for PHE and PYR were close to 80%, once all oxidant was totally consumed.

Comparing runs 10 and 11, where the difference was in the procedure for adding SDS into the media, it was observed that, although similar removal efficiencies of contaminant were achieved at the final reaction time, in the case of run

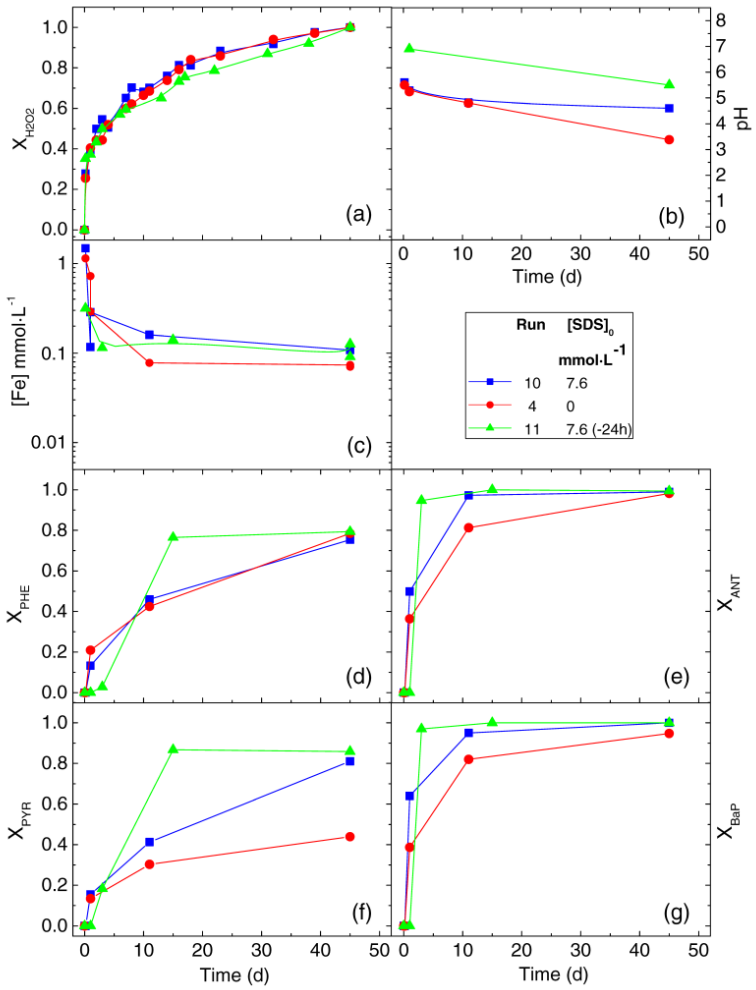

Figure 6. Influence of addition of a surfactant (SDS) to the Fenton's Reagent. Evolution of H_2O_2 conversion (a), pH (b), iron in solution (c). PAHs conversion, PHE (d), ANT (e), PYR (f), and BaP (g). at 20 °C, $V_L/W_{soil} = 2$ mL · g^{-1}, $[Fe]_0 = 1$ mmol L^{-1} as Fe(III) salt, $[H_2O_2]_0 = 882$ mmol L^{-1}.

11, those pollutant conversions were achieved sooner. This comparison confirms the fact that the addition of a surfactant improves the solubilization of contaminants, therefore they can be oxidized faster in the aqueous phase, where the reaction takes place.[17,18]

Transformation products

Under the experimental conditions used, the main aromatic product detected in the oxidation runs was 9–10 anthraquinone (ATQ), confirmed by both HPLC and GC-MS analysis. This transformation product, as reported in the literature, was also found in PAHs oxidation in soil[41,42] and the aqueous phase.[43] Besides, it is supposed that the presence of this byproduct in soil can be temporary, given that it could be biodegraded more easily and quickly than the parent PAH.[41,42] Figure 7 shows the evolution of ATQ with time for all experiments carried out. It is necessary to point out that ATQ appeared in all runs except that in which Fe(III) 5 mmol L^{-1} was added (run 5), which was the run where total removal of all PAHs

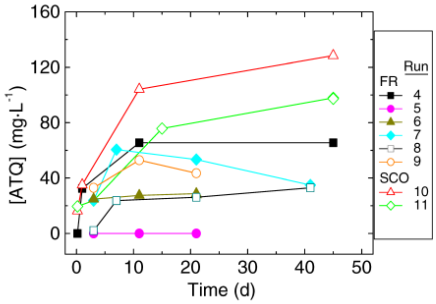

Figure 7. Evolution of ATQ concentration with time in all oxidation reactions (runs 4 to 11).

was achieved. The fact of not having detected ATQ in run 5 means that it was fully degraded as well as the rest of the PAHs, given the strong conditions generated by adding 5 mmol L^{-1} Fe(III).

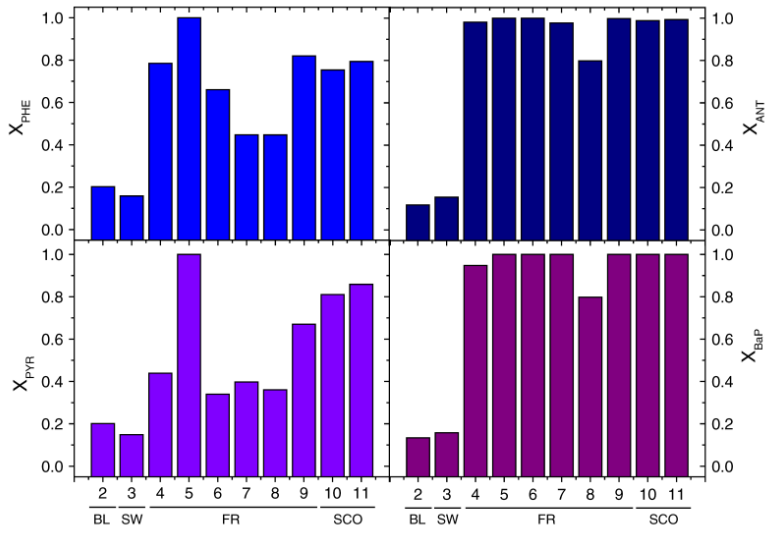

Figure 8. Efficiencies of removal of PHE, ANT, PYR and BaP for all experiments carried out ($t = 48$ days).

Summary of all experiments

Figure 8 shows the corresponding removal efficiencies of each PAH for all experiments at their final reaction time. According to the criteria described in the set-up and procedure section, four groups were established (BL, SW, FR and SCO). In this sense, it is noticed that for both ANT and BaP, almost all techniques applied achieved near total conversions, with lowest conversion of about 80% for run 8 (Fenton reagent with nZVI 5 mmol L^{-1}). On the other hand, lower conversions were reached for PHE and PYR, except for run 5, in which all PAHs were almost completely removed.

CONCLUSIONS

The remediation of a contaminated soil by four different types of PAHs (ANT, PHE, PYR and BaP) by applying Fenton's reagent under different conditions has been investigated. H_2O_2 catalyzed by Fe(III) and nZVI, and also coupled with soil washing with SDS. During reactions the conversion of oxidant, contaminant, concentration of iron in solution and pH were measured.

Natural attenuation and soil washing during the treatment time (48 days) removed less than 20% of the PAHs in soil. In contrast, in the treatments where Fenton reagent was applied, higher removal efficiencies for all PAH were observed. According to the results obtained, PYR and PHE were the PAHs which offered highest resistance to the treatments.

It was found that higher concentrations of iron in solution produced higher PAH and aromatic intermediates removal. pH is a critical factor during treatments with Fenton reagent: with higher acidity higher iron concentration in solution can be obtained. With 1 mmol L^{-1} of iron in solution a time of 5 days was enough to completely eliminate the PAHs and the aromatic intermediates. On the other hand, iron in solution as low as 0.1 mmol L^{-1} was able to catalyze hydrogen peroxide decomposition producing hydroxyl radicals resulting in almost total removal of PAHs in less than 48 days, the controlling step being the hydrogen peroxide lifetime. This iron in solution was obtained by adding an iron salt or nZVI particles. Besides, iron can be extracted from that naturally present in the soil at the pH used. In spite of the addition of nZVI not increasing the PAHs conversion due to the low solubility of iron at the pH used, nZVI can act as a continuous source of iron release.

Addition of the surfactant 24 h prior to the oxidation treatment enhanced PAHs conversion, even if pH was increasing to the neutral range when surfactant was added. This can be attributed to the enhancement in PAHs solubilization and therefore, the increase in oxidation rate in the aqueous phase.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the Comunidad Autonoma de Madrid provided throughout project CARESOIL (S2013-MAE-2739) and from Spanish Ministry of Economy and Competitiveness, projects CTM2010-16693 and CTM2013-43794-R.

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ARTÍCULO 5/ ARTICLE 5

Título/*Title*: Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil.

Autores/*Authors*: Marina Peluffo, Fernando Pardo, Aurora Santos, Arturo Romero.

Estado actual/*current status*: Science of The Total Environment. Septiembre 2016 / *September 2016.* 563–564, 649–656.
Recibido/*Received*: 16-07-2015. Revisado/*Revised*: 04-09-2015. Aceptado para publicación/*Accepted for publication*: 07-09-2015. Publicado Online /*First Published online*: 29-09-2015.

DOI: 10.1016/j.scitotenv.2015.09.034

Factor de impacto/Impact factor (JCR, 2014): 4.099

ARTICLE IN PRESS

STOTEN-18383; No of Pages 8

Science of the Total Environment xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil

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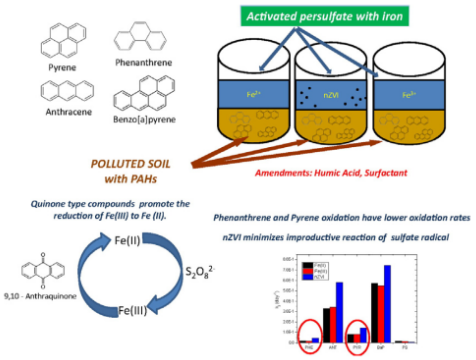
HIGHLIGHTS

- Soil polluted by PAHs was remediated by activated persulfate.
- Iron was added as Fe^{2+}, Fe^{3+} salt or nZVI without pH adjustment.
- Surfactant addition slightly improved PAHs removal efficiencies.
- Quinone type byproducts let Fe^{3+} be reduced to Fe^{2+} improving persulfate activation.
- The highest PAHs conversions were obtained by using nZVI.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 July 2015
Received in revised form 4 September 2015
Accepted 7 September 2015
Available online xxxx

Keywords:
PAHs
Activated persulfate
Zerovalent iron nanoparticles
Surfactant
Soil remediation

ABSTRACT

Contamination of soils by persistent pollutants is considered an important matter of increasing concern. In this work, activated persulfate (PS) was applied for the remediation of a soil contaminated with polycyclic aromatic hydrocarbons (PAHs), such as anthracene (ANT), phenanthrene (PHE), pyrene (PYR) and benzo[a]pyrene (BaP). PS activation was performed by different ways; where ferric, ferrous sulfate salts (1–5 mmol·L^{-1}) and nanoparticles of zerovalent iron (nZVI) were used as activators. Moreover, in order to improve the oxidation rate of contaminants in the aqueous phase, the addition of sodium dodecyl sulfate (SDS), as anionic surfactant, was tested. On the other hand, it was also studied the role of humic acids (HA), as reducing agent or surfactant, on PAHs conversion. Removal efficiencies near 100% were achieved for ANT and BaP in all the runs carried out. Nevertheless, remarkable differences on removal efficiencies were observed for the different techniques applied in case of PHE and PYR. In this sense, the highest conversions of PHE (80%) and PYR (near 100%) were achieved when nZVI was used as activator. Similar results were obtained when activation was carried out either with Fe^{2+} or Fe^{3+}. This can be explained by the presence of quinone type compounds, as 9,10-anthraquinone (ATQ), that can promote the reduction of Fe^{3+} into Fe^{2+}, permitting PS radicals to be generated. On the other hand, the addition of HA

Abbreviations: PS, persulfate; PAHs, polycyclic aromatic hydrocarbons; ANT, anthracene; PHE, phenanthrene; PYR, pyrene; BaP, benzo[a]pyrene; nZVI, nanoparticles of zerovalent iron; SDS, sodium dodecyl sulfate; HA, humic acids; ATQ, 9,10-anthraquinone; SW, soil washing; ISCO, in situ chemical oxidation; NPC, non-productive consumption; BL, blank run; CMC, critical micelle concentration.

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http://dx.doi.org/10.1016/j.scitotenv.2015.09.034

Please cite this article as: Peluffo, M., et al., Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil, Sci Total Environ (2015), http://dx.doi.org/10.1016/j.scitotenv.2015.09.034

did not produce an improvement of the process while surfactant addition slightly increases the PAHs removal. Furthermore, a kinetic model was developed, describing the behavior of persulfate consumption, and contaminants removal under first order kinetics.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are amongst the most widespread organic contaminants in soils, natural waters and wastewater (Puglisi et al., 2007). The release of this compounds into the environment can involve natural phenomenal (e.g. volcanic eruptions, forest fires) or anthropogenic activities (incomplete combustion of fuel, coal, wood, etc.). PAHs are a group of compounds that consist of two or more fused benzene rings (Rivas, 2006), thus, due to their hydrophobic nature and their low solubility in the aqueous phase, these species tend to be adsorbed on solid particulates, especially on the soil organic fractions (Tremblay et al., 2005). Knowing their potentially mutagenic or carcinogenic effects on human and animal health, and their tendency to accumulate in the environment (Tobiszewski and Namiesnik, 2012; Tsapakis and Stephanou, 2005), the removal of this kind of pollutants is considered a priority. In this sense, in order to restore soil and groundwater polluted with PAHs, a wide range of different kinds of treatments have been studied, such as natural attenuation, bioremediation, soil washing (SW) with surfactants and chemical oxidation. Despite natural attenuation is the less invasive technique to manage the remediation of contaminated soils, it is required a long-term monitoring of the soil as well as a deep understanding of the contaminants behavior (Hanser et al., 2015). Bioremediation is a readily available and relatively low cost (in relation to other treatment options) remediation technique for a wide number of organic contaminants, including PAHs (Juhasz et al., 2000; Kanaly and Harayama, 2000; Madueno et al., 2011). However, a general problem for the application of bioremediation on PAH-contaminated soils, lies in the usually rather slow degradation rate of these compounds (Coppotelli et al., 2008). The long time required for the application of bioremediation can be shortened if in situ chemical oxidation (ISCO) is firstly applied (Sakulthaew et al., 2014). ISCO has been increasingly regarded as a relevant alternative to conventional treatment technologies for remediation of groundwater and soils contaminated by recalcitrant organic contaminants (Watts and Teel, 2006), including PAHs (Rivas, 2006; Sirguey et al., 2008). The most commonly used oxidants include permanganate (MnO_4), Fenton's reagent (hydrogen peroxide and Fe^{2+}) (Ferrarese et al., 2008; Laurent et al., 2012; Pardo et al., 2014), ozone (Rivas et al., 2009), and sodium persulfate (PS) (Mora et al., 2014). These oxidants can effectively transform target contaminants in soil or water into harmless products, such as CO_2 and H_2O (Chen et al., 2009). Persulfate has drawn increasing attention as alternative oxidant in the abatement of organic contaminants in the last decade, in fact, persulfate has been recently used for the degradation of organic pollutants in wastewaters (Fang et al., 2013; Kusic et al., 2011; Rodriguez et al., 2012) and is an emerging oxidant for ISCO (Liang et al., 2008). It has several advantages (Tsitonaki et al., 2010) such as high aqueous solubility, high stability at room temperature, relatively low cost and benign end products. Since solubility of potassium persulfate in water is about one order of magnitude lower than that of sodium persulfate, this last is the most common and feasible oxidant form used in ISCO. Persulfate salts dissociate in water to persulfate anions that are strong and relatively stable oxidants (Usman et al., 2012) as shown in Eq. (1):

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}. \quad [1]$$

The use of PS as oxidant has kinetic limitations as it reacts much more slowly than other oxidants. However, when persulfate anion is activated, the sulfate radical ($SO_4^{\cdot -}$), a strong and non-selective oxidant ($E^\circ = 2.6$ V), is produced. In this regard, this activation can be performed through different routes: thermal, photo activation (Eq. (2)) (Johnson et al., 2008) or activation by reduced metal ions, being Fe^{2+} the most commonly used (Eq. (3)) (Osgerby, 2006):

$$S_2O_8^{2-} \xrightarrow{\text{heat or } h\nu} 2SO_4^{\cdot -}, \quad [2]$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot -}. \quad [3]$$

Given the difficulties involved in keeping high temperatures underground (50 °C e.g.), metal activation, in soil natural conditions, is preferred rather than thermal activation. However, in case of metal activation, a termination reaction can involve also undesired non-productive consumption of sulfate radical due to the scavenging of $SO_4^{\cdot -}$ by the activator, Fe^{2+} (Eq. (4))

$$SO_4^{\cdot -} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}. \quad [4]$$

While reaction [4] takes place at high rate, adding an excess of Fe^{2+} would produce a loss of the oxidant. Therefore, the amount and delivery strategy for iron addition becomes a key point in the persulfate treatment (Vicente et al., 2011). In order to solve this disadvantage, the use of ZVI has been proposed in literature, as an alternative to the addition of Fe^{2+} given that ZVI allows a slow release of Fe^{2+} to the aqueous phase, minimizing the extension of reaction. Studies with PS + ZVI concern mainly water treatment (Deng et al., 2014; Liang and Guo, 2010; Liang and Lai, 2008; Oh et al., 2009) and to a lower extent soil treatment (Oh and Shin, 2014), where a ZVI powder was used as activator of persulfate for the treatment of a diesel-contaminated soil. To solve the suitability of the injection of ZVI in geological porous the use of ZVI in the form of nanoparticles has been studied (Al-Shamsi and Thomson, 2013).

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + SO_4^{2-}. \quad [5]$$

As can be deduced from Eq. (3), Fe^{2+} is required to form sulfate radicals. However, as can be observed in Eq. (3), Fe^{2+} is oxidized to Fe^{3+}. Therefore, it would be required the reduction of Fe^{3+} to Fe^{2+} to let the sulfate radical generation continue. In some cases, this reduction can be produced by the organic pollutants in the media, which can be either original pollutants or organic oxidation intermediates which appear during reaction, like quinone type compounds (Rodriguez et al., 2014). On the other hand, the addition of some compounds, like humic acids, could enhance this reduction. In this regard, it has been reported the ability of humic substances to reduce Fe^{3+} to Fe^{2+} in the aqueous phase, thus improving the application of chemical oxidation techniques (Fukushima and Tatsumi, 1999; Voelker et al., 1997). Moreover, humic substances (HA), have been described as naturally occurring surfactants, begin to be recognized as a possible aid in soil bioremediation techniques (Conte et al., 2005; Conte et al., 2001). The bioavailability of PAH appeared to be increased by addition of exogenous humic substances to contaminated soils (Holman et al., 2002). An enhancement of the solubility of the pollutants in the aqueous phase could increase the oxidation rate of the hydrophobic compounds because the sulfate radical is produced in the aqueous phase. Surfactants are surface-active agents which lower the surface tension of a liquid and also decrease the interfacial tension between two immiscible liquids. Chemical surfactants increase the solubility of PAHs (Mesbaiah et al., 2014; Wang et al., 2013), and consequently facilitate their further oxidation in the aqueous phase. These surface active agents, either anionic or no-ionic, have been used

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widely for the remediation of PAHs-contaminated soils (Cheng and Wong, 2006; Peng et al., 2011; Saxe et al., 2000; Zhou and Zhu, 2005). Particularly, in this work, it has been selected the use of sodium dodecyl sulfate, an anionic surfactant, due to its biodegradability and low adsorption degree to the soil surface (Giannis et al., 2007). Application of surfactants in field can be carried out by two different ways, in series, injecting firstly the surfactant and treating subsequently the washed flow with chemical oxidation, or in parallel, where surfactant and oxidant are injected simultaneously in the contaminated soil (Wang et al., 2013). Therefore, the aim of this work is to study the remediation of a fresh spiked soil by 4 PAHs, anthracene (ANT), phenanthrene (PHE), pyrene (PYR) and benzo[a]pyrene (BaP), all included in the 16 PAHs priority list made by the EPA, by using persulfate activated with iron. Three types of iron addition have been considered: Fe^{2+}, Fe^{3+} and nZVI particles in order to analyze their importance on reactions in Eqs. (3)–(5). Besides, it was tested the addition of sodium dodecyl sulfate (SDS) as surfactant and HA. Analyses of contaminant and oxidant conversion and soil pH were studied along 40 days of treatment. In addition, a kinetic model was proposed for the description the behavior of the oxidant consumption and contaminants conversion. The presence and role of aromatic intermediates during reaction was also studied.

2. Material and methods

2.1. Reagents

Phenanthrene (PHE) ≥99.5% (sublimed grade), ref. 695114, from Aldrich (France), anthracene (ANT) 99% (ReagentPlus), ref. 141062, from Aldrich (France), Pyrene (PYR) 98%, ref. 185515, from Aldrich (France) and Benzo[a]pyrene (BaP) ≥96%, ref. B1760, from Sigma (France) were used for soil spiking and HPLC analysis. Sodium PS ≥98%, used as oxidant, was purchased from Sigma-Aldrich; ferric sulfate from Panreac 75% (anhydrous basis); ferrous sulfate heptahydrate ≥99%, from Fisher, and air-stable nZVI powder (NANOFER STAR) from Nanoiron s.r.o. were used, respectively, as activator species. For SW and coupled SW with activated persulfate it was used SDS ≥99%, from Sigma-Aldrich, as surfactant. As HA source it was used a HA sodium salt (45–70%), provided by Acros Organics. For persulfate determination, reagents required were sodium hydrogen carbonate 99.7% (Panreac), potassium iodide >99.5% (Fisher Chemical) and sodium thiosulfate pentahydrate 99.5% (Sigma-Aldrich). Sodium sulfate anhydrous 99%, from Fisher Chemical, Acetone 99.8% HPLC gradient grade from Fisher Chemical and n-hexane 99% HPLC grade from Scharlab were used for contaminant extraction from the soil samples. Dichloromethane ≥99.8% HPLC grade from Sigma-Aldrich for the analysis of intermediates. Phosphoric acid ≥85% from Sigma-Aldrich and acetonitrile HPLC gradient grade from Fisher Chemical were both used as mobile phase in HPLC for PAH analysis. For metal determination in aqueous solution in MP-AES analysis, nitric acid 69.5% was employed for the stabilization of iron ions.

2.2. Soil spiking

A sandy clay loam BT horizon (pH = 7.22; total organic carbon = 0.196%, free iron oxides = 7235 $mg \cdot kg^{-1}$) from the Autonomous Community of Madrid was used for spiking. Its characterization procedure and a detailed description of the properties are found elsewhere (Pardo et al., 2014; Vicente et al., 2012). Procedure of soil spiking was performed as followed in literature (Kulik et al., 2006; Mora et al., 2014), where an acetone solution with ANT, PHE, PYR and BaP was distributed and mixed manually onto the soil with a spatula. Contaminant concentrations obtained were 97 ± 6 $mg \cdot kg^{-1}$ for ANT, 89 ± 2 $mg \cdot kg^{-1}$ for PHE, 93 ± 1 $mg \cdot kg^{-1}$ for PYR and 102 ± 1 $mg \cdot kg^{-1}$ for BaP, respectively.

2.3. Set-up and procedure

All runs, in batch mode, were performed under isothermal stirring (Unitronic orbital shaker by Selecta) at 100 rpm and 20 °C, without pH adjustment, employing 50 mL PTFE centrifuge tubes with PTFE screw caps, placed horizontally. Each time point was represented by one PTFE tube, where 10 mL of aqueous solution (V_L) were added to 5 g of polluted soil (W_{soil}). This ratio was selected in order to simulate the removal of PAHs entrapped into soil pores or SOM present in the saturated or vadose zones and treatment can be applied both In Situ or Off Site after excavation. All remediation runs were carried out in duplicate. The non-productive consumption of oxidant (NPC) in this soil was studied in a previous work (Pardo et al., 2015) finding that about 20% of the oxidant was consumed after 83 days and 10% of initial PS was remaining after 20 days. Oxidation runs carried out are summarized in Table 1. A blank run (BL) without addition of oxidant in the aqueous phase and a SW run using an aqueous solution of SDS were carried out in order to determine the natural attenuation and the PAHs eluted by the surfactant in the period time studied (about 50 days).

Runs using PS as oxidant were carried out by using several types of iron (ferric, ferrous sulfate salts (1–5 $mmol \cdot L^{-1}$) and nanoparticles of zerovalent iron (nZVI)). On the other hand, two runs consisted in the addition of either HA or surfactant, SDS was added at its critical micelle concentration (CMC), being 2.2 $g \cdot L^{-1}$ (20 °C) (Dahanayake et al., 1986; Watanabe et al., 2005), 24 h before PS addition. Humic Acids, HA, were added at a concentration of 2000 $mg \cdot kg^{-1}$. At the selected reaction time, two centrifuge tubes were sacrificed (differences lower than 15%). Afterwards, aqueous and soil phase were separated by centrifugation, analyzing pH, remaining oxidant, surfactant and metals in solution in the aqueous phase. In addition, PAHs and oxidation by-products were extracted as reported in previous works (Pardo et al., 2014), by following the EPA method 3540C, where Soxhlet extraction was used. For oxidation by-products identification, hexane and acetone were evaporated in a fume hood, after solvent extraction, at room temperature and reconstituted in 2 mL dichloromethane, analyzing afterwards in GC/MS.

2.4. Analytical method

The concentration of PS in solution was determined by iodometric titration with a solution of sodium thiosulfate, $Na_2S_2O_3$, 0.3 g/L, by using a combined-Pt ring electrode, specific for redox titrations, supplied by Metrohm, ref. 6.0451.100. pH was measured with a pH glass electrode also supplied by Metrohm. For the analysis of iron a microwave plasma-atomic emission spectrometer 4100 MP-AES (Agilent Technologies) with OneNeb nebulizer was used. The selected wavelength for iron determination was 259.94 nm. Oxidation byproducts were analyzed by GC/MS (HP 6890N MSD 5975B). For original PAHs determination, an HPLC (Agilent, mod. 1100) coupled with an Agilent 1290 Infinity Diode Array Detector was employed. The column used was a Poroshell 120 SB-C18 in 2.1 mm × 100 mm and 2.7 μm of particle size. Analysis was carried out under isocratic mode at a flow rate of 0.5 $mL \cdot min^{-1}$, selecting as mobile phase a mixture of 60% acetonitrile

Table 1
Experimental runs.

Run	Fe (type)	C Fe_0 $mmol \cdot L^{-1}$	C AH $mg \cdot L^{-1}$	C_{SDS} $g \cdot L^{-1}$
RPS1	II	1	0	0
RPS2	III	1	0	0
RPS3	nZVI	1	0	0
RPS4	II	1	0	2.2
RPS5	nZVI	1	0	2.2
RPS6	II	1	2000	0
RPS7	nZVI	5	0	0
BL	0	0	0	0
WS	0	0	0	2.2

C_{PS0} = 50,000 $mg \cdot L^{-1}$, $C_{PAH} \approx$ 100 $mg \cdot kg^{-1}$ each, T = 20 °C, W_{soil}/V_L = 0.5 $g \cdot cm^{-3}$.

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and 40% aqueous solution with phosphoric acid 75 mmol·L^{-1}, selected injection volume was 20 μL. Wavelength chosen were, 235 nm for PYR, 250 nm for PHE, and 295 nm for ANT and BaP. The presence of reaction intermediates was analyzed by GC/MS (HP 6890 N MSD 5975B). A HP-5 column (30 m × 0.32 mm i.d. × 0.25 μm) was used for the analysis. The chromatographic conditions were as follows: injector temperature: 280 °C; carrier gas (He) flow rate: 2 mL·min^{-1}; 8 μL of injected volume in splitless mode. The analysis was performed with an initial oven temperature: 45 °C, followed by a first ramp of 5 °C·min^{-1} to 150 °C and a second ramp of 8 °C·min^{-1} to 325 °C. The final run time was 62.88 min. The corresponding detection limits for PAHs were 0.27 mg·L^{-1} for PHE, 0.11 mg·L^{-1} for ANT, 0.37 mg·L^{-1} for PYR and 0.47 mg·L^{-1} for BaP.

3. Results and discussion

The effect of type and concentration of iron added (runs RPS1, RPS2, RPS3, RPS7), the influence of surfactant (runs RPS4 and RPS5) and HA addition (run RPS6 and RPS5), on PAHs conversion, oxidant consumption and pH evolution have been analyzed. PAH and oxidant conversions have been calculated according to Eq. (6).

$$X_j = \frac{C_0^j - C_t^j}{C_0^j}. \quad [6]$$

Being X_j the conversion of contaminant or oxidant; C_0^j the initial concentration of a certain PAH or oxidant; C_t^j the concentration of PAH or oxidant at a time t.

Although PAHs were analyzed in both aqueous and solid phases (after extraction), the amount of these compounds in aqueous phase was negligible, in comparison with that remaining in the soil phase. Besides, the PAHs remaining in soil after 50 days of washing with distilled water or water with 2.2 g·L^{-1} of SDS was higher than 80% of their initial concentration. Moreover, negligible conversion of each of the PAHs was observed when PS (200 mmol·L^{-1}) was added alone.

3.1. Effect of type of iron added

As it was previously cited, iron was added as Fe^{2+}, Fe^{3+} or nZVI. Fig. 1 shows the results obtained when PS 200 mmol·L^{-1} and iron 1 mmol·L^{-1} were added to the polluted soil. PHE, ANT, PYR and BaP conversion are showed in Fig. 1a to d, respectively. PS consumption is plotted in Fig. 1e, while the non-productive consumption of the oxidant (without PAHs and iron addition) is also presented in Fig. 1e. As can be seen, PHE is the most recalcitrant PAH to persulfate oxidation, in the three runs showed in Fig. 1, followed by PYR. On the contrary, it was observed that ANT and BaP were quite readily oxidized. According to literature, this kind of trend is consistent with those works in which fresh spiked soils have been treated with chemical oxidation; on one hand, the way BaP, with the higher number of benzene rings (5), was the contaminant more easily degraded can be explained by, firstly, it may take more time to reach and bind with the soil organic matter than the rest of PAH (3 and 4 rings), thus its availability for the oxidant would be higher (Bogan and Trbovic, 2003). In addition, reactivity of PAHs towards oxidation, apart from absorption phenomena, reaction conditions, etc. generally increases with the number of aromatic rings, since less energy is needed to form the oxidation products (Forsey et al., 2010; Lemaire et al., 2013). Regarding ANT degradation, which is faster than PHE and PYR, it may be also explained by the lower energy that would be needed to form a highly stable oxidation product, as is 9,10-anthraquinone (ATQ) (Forsey et al., 2010). No differences were found regarding the source of iron added, as a ferrous or ferric salt, indicating that Fe^{3+} can be reduced by species in the reaction media. On the contrary, the addition of Fe as nZVI remarkably improved the abatement of both PHE and PYR while diminish slightly the PS consumption. This could be explained if nZVI produce a slow release of iron minimizing the radical scavenger in Eq. (4). In this sense, some works have reported this behavior, confirming that better results have been obtained with the use of nZVI against Fe^{2+} as persulfate activator, for the removal of a biodiesel-blend from a contaminated soil (Pardo et al., 2015), TCE (Al-Shamsi and Thomson, 2013) or 2,4-dichlorophenol (Li et al., 2015). As can be seen in Fig. 1e, PS consumption was about 60% after 50 days of reaction when Fe^{2+} or Fe^{3+} were added, while it remains at 40% for nZVI addition. In Fig. 1e it is also shown the non-productive consumption of PS for an unpolluted soil in absence of iron addition, being about 15% after 50 days. As the reaction progress, the acidification of the soil takes place, obtaining similar pH profiles for the three types of iron used, as can be seen in Fig. 1f.

3.2. Effect of the surfactant and HA addition

Effect of surfactant addition is shown in Fig. 2. PHE and PYR conversion are showed in Fig. 2a and b, respectively. PS consumption is showed in Fig. 2c and pH profile in Fig. 2d. A slight increase when using SDS was noticed for ANT and BaP conversion (not shown), this increase was difficult to quantify due to the high oxidation rate of both compounds with activated PS. As can be seen in Fig. 2a, the addition of SDS 24 h before PS an iron are supplied increases the PHE conversion. A lower effect of the surfactant is noticed on PYR conversion; probably due to PYR has a higher oxidation rate than PHE in absence of surfactant. Addition of SDS produces also a slight increase in the PS consumption (Fig. 2c), and has no effect on the pH evolution. This increase in PS consumption is probably due to the partial oxidation of the surfactant.

Effect of HA addition was analyzed by comparison of results obtained in runs RPS1 and RPS6. Effect on PHE and PYR conversion is showed in Fig. 3a. PS consumption obtained in both runs is plotted in Fig. 3b. As can be seen, no differences are obtained in presence of HA. Profiles of ANT, BaP and pH obtained in run RPS6 were also closed to those obtained in RPS1. In literature is reported the redox activity of some components presents in HA, such as quinone type compounds (Kappler et al., 2004; Tsang et al., 2009), which could help to improve the application of ISCO techniques by enhancing the reduction of Fe^{3+} to Fe^{2+} in the aqueous phase (Fukushima and Tatsumi, 1999; Voelker et al., 1997). Besides, HA can also act as surfactants, increasing the concentration of contaminants in the aqueous phase (Conte et al., 2005). In this case, the positive effect of HA was not observed. This can be explained because a lower amount of HA was used, moreover not all the compounds present in the HA have the ability of reducing iron, and also due to the fact that the oxidation intermediates of PAHs can reduce Fe^{3+} to Fe^{2+}. In fact, quinone type compounds, as ATQ, were detected as the main aromatic intermediate if PS was used. This explains the similar results obtained with Fe^{2+} and Fe^{3+} in runs RPS1 and RPS2. Besides, the presence of HA can also decrease the removal efficiency of contaminants, given that they can adsorb the contaminants decreasing their availability because of an increase in the number of hydrophobic sites (Bogan and Trbovic, 2003; Conte et al., 2001), besides, they can consume oxidant, increasing its non-productive consumption, as it was seen in the treatment of an ANT contaminated soil by using ozonation (Zhang et al., 2005).

3.3. Effect of iron concentration

Effect of concentration of initial iron added was studied by using 1 and 5 mmol·L^{-1} nZVI (runs RPS3 and RPS7). Effect on PHE and PYR conversion is showed in Fig. 4a. PS consumption obtained in both runs is plotted in Fig. 4b. Profiles of ANT, BaP and pH obtained in runs RPS3 and RPS7 were similar to those obtained in runs RPS3 and RPS7 (showed in Fig. 1). As can be seen in Fig. 4, the increase of nZVI concentration, at the range studied, produces a slight increase in the PHE conversion but an almost negligible effect on the PYR conversion. On the contrary, PS consumption is remarkable increased. According to Eq. (3), the higher the iron concentration, the higher the PS consumption,

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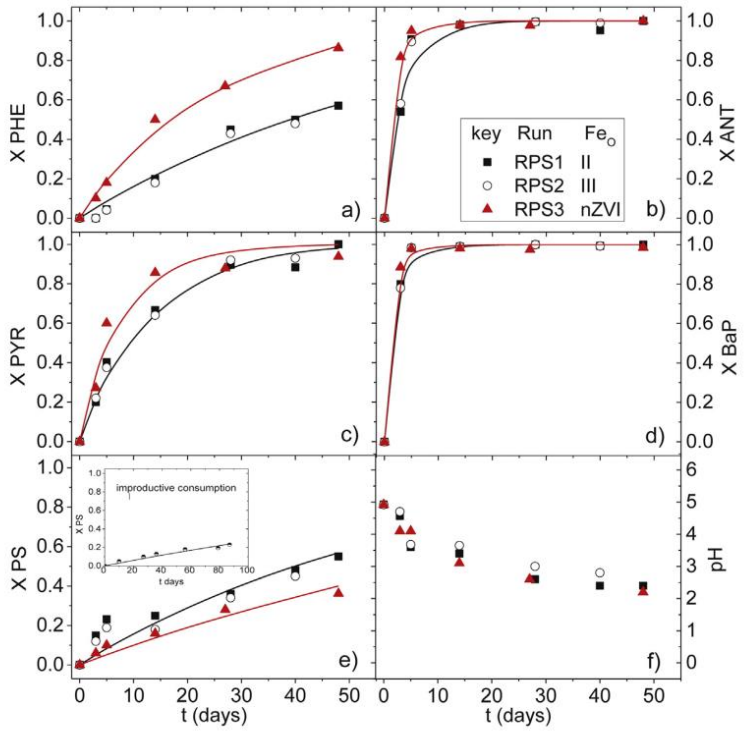

Fig. 1. Effect of type of iron initially added on a) PHE b) ANT, c) PYR, d) BaP, e) PS conversion and f) pH profile. $[Fe]_0 = 1$ mmol·L^{-1} $[PS]_0 = 50{,}000$ mg·L^{-1} $[PAH]_j \approx 100$ mg·kg^{-1}. Runs RPS1, RPS2 and RPS3 using Fe^{2+}, Fe^{3+} and nZVI, respectively. Symbols: experimental data. Lines: estimated values with Eq. (7) using parameters in Table 2.

then explaining the higher persulfate consumed at 5 mmol · L^{-1} nZVI. Small effect of nZVI concentration on PAH conversion (in the range studied) can be explained by the scavenging reaction between iron and sulfate radical given in Eq. (4). As the PS/Fe molar ratio increases, the removal efficiency of contaminants can increase; nevertheless, this improvement can be hindered due to scavenging reactions from an excess of Fe^{2+} which reacts with sulfate radicals, as has been reported in literature (Al-Shamsi and Thomson, 2013; Rodriguez et al., 2012; Vicente et al., 2011).

3.4. Kinetic model

As a significant amount of the initial PS remains in the media after oxidation of PAHs, the oxidation rate of each PAH has been described

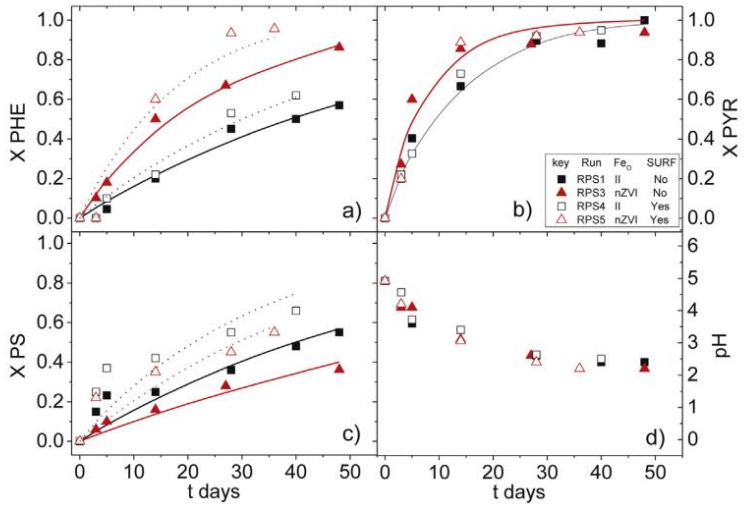

Fig. 2. Effect of surfactant addition on a) PHE b) PYR c) PS conversion and d) pH profile. $[Fe]_0 = 1$ mmol·L^{-1} $[PS]_0 = 50{,}000$ mg·L^{-1} $[PAH]_j \approx 100$ mg·kg^{-1}. Runs RPS1 and RPS3 without surfactant. Runs RPS4 and RPS5 with surfactant. Symbols: experimental data. Lines: estimated values with Eq. (7) using parameters in Table 2.

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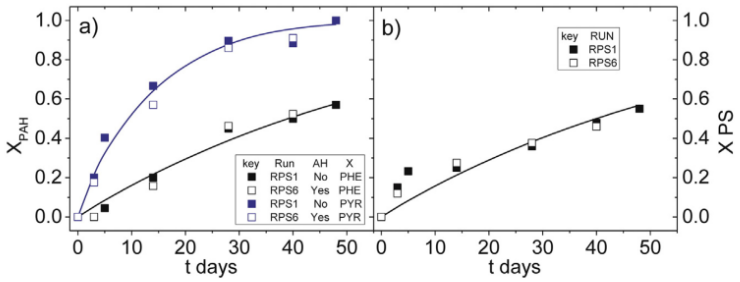

Fig. 3. Effect of HA addition on a) PHE and PYR b) PS conversion $[Fe]_0 = 1$ mmol·L^{-1} $[PS]_0 = 50{,}000$ mg·L^{-1} $[PAH]_j \approx 100$ mg·kg^{-1}. Run RPS1 without HA, run RPS6 with HA addition. Symbols: experimental data. Lines: estimated values with Eq. (7) using parameters in Table 2.

by using a first order reaction rate. Given that all runs have been carried out in batch way, the integrated expression for each PAH conversion results as follows:

$$X_{PAHj} = 1 - \exp(-k_j t). \quad (7)$$

The PS disappearance rate has been described by a first order reaction on PS concentration, with two contributions, a first one due to the non-productive consumption of PS for the unpolluted soil and a second contribution which considers the activation by iron at the experimental conditions used in each run, being the integrated equation as follows:

$$X_{PS} = 1 - \exp(-(k_{unp} + k_{PSFe})t). \quad (8)$$

The value of k_{unp} was obtained by fitting X_{PS} vs time, obtained with clean soil and no iron addition, getting a value of $k_{unp} = 0.0031$ day^{-1}, which reproduce accurately the experimental data in Fig. 1e (symbols as experimental data, line as estimated value).

Kinetic constants in Table 2 were obtained by fitting each PAH conversion vs time and PS conversion vs. time to Eqs. (7) and (8), from each run. From the prediction of the PAH conversion values (plotted as lines in Figs. 1 to 4), calculated with the kinetic constants in Table 2, a good agreement between estimated an experimental values was obtained. As shown in Table 2, the higher kinetic constants for the degradation of all PAHs, corresponded to nZVI addition, while those calculated for the initial addition of Fe^{2+} or Fe^{3+} were lower. In this regards, it was noticed that this effect was more remarkable for PHE and PYR degradation, since these compounds are the more recalcitrant to chemical oxidation by using activated persulfate. In this sense, Forsey et al. (2010) found for permanganate oxidation of PAHs, that PYR constant of degradation was higher than that corresponding for PHE. On the other hand, Al-Shamsi and Thomson (2013) also determined the kinetic constants corresponding to TCE degradation by persulfate activated by Fe^{2+} and nZVI, finding out faster removal rates for the contaminant when nZVI was used rather than Fe^{2+}. Nevertheless, it is frequently observed, regarding treatments with nZVI-activated persulfate, a first stage where oxidant and contaminants are more quickly consumed, and a second lower one, due to passivation or deactivation of nZVI surfaces.

4. Conclusions

This study has provided valuable data in regard to the application of different kinds of persulfate activation for the remediation of a PAH contaminated soil with four different types of PAH, ANT and PHE (3-ringed) PAH, PYR (4-ringed) and BaP (5-ringed). For persulfate activation it was tested the effect of the type of iron species initially added (Fe^{3+} or Fe^{2+} sulfate salt and nZVI), concentration of nZVI and the addition of HA and surfactant. Evolution of species during reaction was carried out through the analysis of oxidant consumption, PAHs conversion and pH with time. It was observed that ANT and BaP were degraded near totally in all runs, while in case of PHE and PYR, different removal efficiencies were achieved depending on the technique used. In this sense, PHE and PYR removal efficiencies have been considered as crucial parameters in order to compare the effectiveness of each remediation technique applied. Thus, according to the type of iron initially added, best removal efficiencies, after 48 days, were achieved when nZVI was added, 86% for PHE and 99% for PYR, while for Fe^{2+} (57% PHE, 95% PYR) or Fe^{3+} (51% PHE, 93% PYR) were lower. The improvements found with nZVI, are due to the fact that it acts as a continuous release source of Fe^{2+}. Therefore sulfate radicals are produced in a more controlled way, thus minimizing the unproductive sulfate radical consumption noticed when same amount of iron was added as Fe^{2+}. The addition of Fe^{3+} leaded also to persulfate activation due to the appearance of quinone type organic compounds, as degradation products from their parent compounds, like ATQ, capable of reduce Fe^{3+} to Fe^{2+}, and consequently, activate persulfate. Regarding effect of surfactant addition, it was observed a slight improvement in the PAHs removal as a consequence of an increase in the mass transfer from the soil to the aqueous phase due to the solubilization. It is important to mention that, since it has been

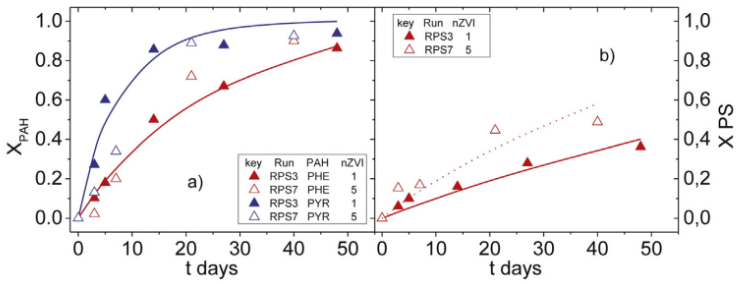

Fig. 4. Effect of nZVI concentration on a) PHE and PYR b) PS conversion $[PS]_0 = 50{,}000$ mg·L^{-1} $[PAH]_j \approx 100$ mg·kg^{-1}. Symbols: experimental data. Lines: estimated values with Eq. (7) using parameters in Table 2.

Please cite this article as: Peluffo, M., et al., Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil, Sci Total Environ (2015), http://dx.doi.org/10.1016/j.scitotenv.2015.09.034

Table 2
Estimated kinetic constants for runs in Table 1. Kinetic model in Eqs. (6) and (7).

Run art	Fe (type)	C Fe_0 $mmol \cdot L^{-1}$	C AH $mg \cdot L^{-1}$	C_{SDS} $g \cdot L^{-1}$	k_{PHE} day^{-1}	k_{ANT} day^{-1}	k_{PYR} day^{-1}	k_{BaP} day^{-1}	k_{PSFe} day^{-1}
RPS1	II	1	0	0	$1.79 \cdot 10^{-2}$	$3.30 \cdot 10^{-1}$	$8.24 \cdot 10^{-2}$	$5.74 \cdot 10^{-1}$	$1.44 \cdot 10^{-2}$
RPS2	III	1	0	0	$1.69 \cdot 10^{-2}$	$3.41 \cdot 10^{-1}$	$8.15 \cdot 10^{-2}$	$5.48 \cdot 10^{-1}$	$1.25 \cdot 10^{-2}$
RPS3	nZVI	1	0	0	$4.33 \cdot 10^{-2}$	$5.79 \cdot 10^{-1}$	$1.43 \cdot 10^{-1}$	$7.45 \cdot 10^{-1}$	$7.58 \cdot 10^{-3}$
RPS4	II	1	0	2.2	$2.36 \cdot 10^{-2}$	$3.77 \cdot 10^{-1}$	$8.73 \cdot 10^{-2}$	$6.53 \cdot 10^{-1}$	$3.14 \cdot 10^{-2}$
RPS5	nZVI	1	0	2.2	$6.80 \cdot 10^{-2}$	$6.83 \cdot 10^{-1}$	$1.14 \cdot 10^{-1}$	$1.20 \cdot 10^{0}$	$2.11 \cdot 10^{-2}$
RPS6	II	1	2000	0	$1.85 \cdot 10^{-2}$	$2.75 \cdot 10^{-1}$	$6.38 \cdot 10^{-2}$	$5.74 \cdot 10^{-1}$	$1.42 \cdot 10^{-2}$
RPS7	nZVI	5	0	0	$4.95 \cdot 10^{-2}$	$1.73 \cdot 10^{-1}$	$7.37 \cdot 10^{-2}$	$5.12 \cdot 10^{-1}$	$1.87 \cdot 10^{-2}$

carried out the remediation of a fresh spiked soil, regardless the technique applied, all these PAHs conversions obtained can present some overestimation compared to those obtained when aged soils were treated. Nonetheless, the effect of using surfactant in case of aged soils could have been more remarkable. On the other hand, no significant improvement was noticed when HA were added. This can be due to the production of quinone type compounds as oxidation by-products from PAH, acting as Fe^{3+} reducers. The effect of reducing species present in the HA can be hidden by these quinone intermediates. In this sense, a higher concentration of HA could be tested in further research in order to verify this point. When iron was added at different concentrations, it was observed a more significant effect on persulfate consumption rather than the removal efficiency of the PAHs, the scavenging reactions between sulfate radicals and iron could have been hinderer the efficiency of the process. PAHs removal efficiencies were estimated accurately following a pseudo first order kinetics, on the other hand. PS consumption was also described by first order kinetics, but with two contributions, one related to the non-productive consumption and the other to the activation by iron. Therefore, this work has provided valuable data, in lab scale, with regard to the activation of persulfate, a useful tool of increasing implementation in field scale for the remediation of contaminated soils, outlining the benefits of adding nZVI as activator, which works as a continuous release source of iron, minimizing the sulfate radical scavenging by an excess of Fe^{2+}.

Acknowledgments

The authors acknowledge the financial support from the Comunidad Autonoma de Madrid provided through the project CARESOIL (S2013-MAE-2739) and from the Spanish Ministry of Economy and Competitiveness, grant BES2011-044329 and project CTM2013-43794-R.

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Please cite this article as: Peluffo, M., et al., Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil, Sci Total Environ (2015), http://dx.doi.org/10.1016/j.scitotenv.2015.09.034

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Please cite this article as: Peluffo, M., et al., Use of different kinds of persulfate activation with iron for the remediation of a PAH-contaminated soil, Sci Total Environ (2015), http://dx.doi.org/10.1016/j.scitotenv.2015.09.034

ARTÍCULO 6/ ARTICLE 6

Título/*Title*: Fate of iron and polycyclic aromatic hydrocarbons during the remediation of a contaminated soil using iron-activated persulfate: a column study

Autores/*Authors*: Fernando Pardo, Aurora Santos, Arturo Romero.

Estado actual/*current status*: Science of The Total Environment. Octubre 2016 / *October 2016*. 566-567:480-8.
Recibido/*Received*: 09-03-2016. Revisado/Revised: 25-04-2016. Aceptado para publicación/*Accepted for publication*: 29-04-2016. Publicado Online/*Published online*: 25-05-2016.

DOI: 10.1016/j.scitotenv.2016.04.197

Factor de impacto/Impact factor (JCR, 2014): 4.099

Science of the Total Environment 566–567 (2016) 480–488

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Fate of iron and polycyclic aromatic hydrocarbons during the remediation of a contaminated soil using iron-activated persulfate: A column study

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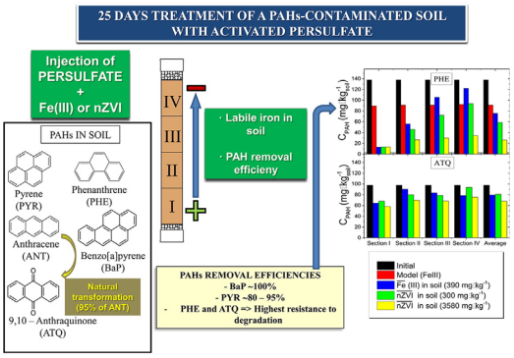
HIGHLIGHTS

- A PAH-contaminated soil was treated under flow conditions with activated persulfate.
- Fe(III) and nZVI were used for persulfate activation, being nZVI more efficient.
- PAH conversions were higher in the nearer sections of the injection point.
- Transport of iron across the column length was related to removal efficiency.
- The oxidation byproduct, anthraquinone, was more resistant than the rest of PAH.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 March 2016
Received in revised form 24 April 2016
Accepted 29 April 2016
Available online xxxx

Editor: Jay Gan

Keywords:
Activated persulfate
Column
PAHs
Anthraquinone

ABSTRACT

Remediation of contaminated soils under flow-through conditions is an issue of great interest since it provides a better approach to real case applications than batch experiments. In this work, a column filled with soil, artificially spiked and aged for three months with Phenanthrene (PHE), Anthracene (ANT), Pyrene (PYR) and Benzo(a)pyrene (BaP), was treated for 25 days with persulfate (PS) activated by Fe^{3+} and nanoparticles of zerovalent iron (nZVI). Effects of type of iron fed into the column (Fe^{3+} or nZVI) and nZVI concentration were studied. PS inlet concentration was 0.2 mmol cm^{-3} and residence time in the column was close to 1.72 days. Iron, PS and polycyclic aromatic hydrocarbons (PAHs) concentration, as well as pH, were monitored during treatment. Concentration profiles of iron and PAHs were observed along the column, with higher iron concentrations and higher PAHs removal efficiencies in the closest sections to the column entrance. BaP and ANT were completely depleted regardless the conditions used, but PHE and PYR showed higher resistance to oxidation, achieving near a 90% removal in the closest sections to the injection source in all runs, but decreasing significantly with column length. Besides, natural degradation of ANT resulted in the formation 9.10-anthraquinone (ATQ), an oxy-

Abbreviations: *PHE*, phenanthrene; *ANT*, anthracene; *PYR*, pyrene; *BaP*, benzo(a)pyrene; *PS*, persulfate; *nZVI*, nanoparticles of zerovalent iron; *PAH*, polycyclic aromatic hydrocarbons; *ATQ*, anthraquinone; *oxy-PAHs*, oxidized species from PAHs; *ISCO*, in situ chemical oxidation; $q_{Fe\ col}$, average amount of iron retained in the column (mg cm^{-3}); V_{col}, column volume (cm^3); *Q*, inlet flow rate ($cm^3\ day^{-1}$); C_{Fe0}, initial concentration of iron in the inlet flow (mg cm^{-3}); C_{Fe}, concentration of iron measured at the exit of the column (mg cm^{-3}); t_{ini}, time in which iron was added initially (days); t_{delay}, time corresponding to the residence time in the column (days); N_{PS}, mmol of persulfate consumed (mmol $kg^{-1}\ day^{-1}$); C_{PS0}, initial concentration of persulfate in the inlet flow (mmol cm^{-3}); C_{PS}, concentration of persulfate measured at the exit of the column (mmol cm^{-3}); *-Ip*, ionization potential; *HOMO*, highest occupied molecular orbital; C_{PAH}, concentration of PAH in soil ($mg_{PAH}\ kg_{soil}^{-1}$).

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http://dx.doi.org/10.1016/j.scitotenv.2016.04.197

Fe^{3+}
nZVI

PAH which showed higher resistance than PHE and PYR. Although higher PAHs removal efficiencies were achieved when nZVI was used as activator, only a moderate improvement was noticed when the highest concentration of nZVI was used as a consequence of radical scavenging by an excess of Fe^{2+}. Finally, a kinetic model based on runs performed in batch, from a previous work, was able to predict the experimental average concentrations of PAHs in the column when Fe^{3+} was used as activator.

1. Introduction

For decades, Polycyclic Aromatic Hydrocarbons (PAHs) have appeared and accumulated in soils and groundwater, becoming one of the most widespread contaminants in the world (Peluffo et al., 2015; Puglisi et al., 2007). Soil and groundwater contamination by PAHs is a consequence of the development and growth of several industrial activities, such as those related to manufacture gas plants, wood impregnation, coke manufacturing, hydrocarbon production and metal processing, (Brown et al., 2003; Sims and Overcash, 1983), as well as diverse natural phenomena (volcano eruptions, forest fires). PAHs are organic species composed of two or more aromatic fused benzene rings, possessing very low solubility in water (lipophilicity), low volatility and high solid-water partition coefficient which makes them interact easily with soil organic matter, decreasing their availability to microorganisms or to degrading agents, thus tending to accumulate in soils (Hamdi et al., 2006). Given that PAHs have been proven to possess carcinogenic and mutagenic potential (e.g. benzo(a)pyrene), most of them are included in the 16 priority pollutants list made by the EPA. Furthermore, not only the original PAHs present in soil, but their corresponding oxidized species, mainly the quinone species, known as oxy-PAHs, represent a serious risk. In fact, Oxy-PAHs are more soluble in water and possess higher mobility in the aqueous phase than their corresponding parent PAH. Therefore, given their similar toxicity and harmful effects to human health as well as their higher stability to degradation than the parental PAH, oxy-PAHs may be even more dangerous than PAHs (Lundstedt et al., 2007; Rodgers-Vieira et al., 2015). Regarding PAHs removal from contaminated soils or groundwater, there is a wide variety of different techniques that can be applied, such as natural attenuation (Biache et al., 2011; Hanser et al., 2015), biostimulation (Hwang and Cutright, 2002; Liebeg and Cutright, 1999), bioaugmentation (Juhasz et al., 2000; Madueno et al., 2011; Rockne et al., 1998) or even the application of bio barriers (Ferreira et al., 2013; Thiruverikatachari et al., 2008). Unfortunately, these techniques require long-term control and application and it is rather frequent that contaminants remain strongly bonded to the soil organic matter, resulting in bioavailability limitations that decrease the effectiveness of their application, hindering to reach the cleanup goals (Antizar-Ladislao et al., 2005; Mahmoudi et al., 2013). In this sense, the application of In Situ Chemical Oxidation (ISCO) techniques has shown good results for the removal of several organic contaminants, as in the case of PAHs, by applying permanganate oxidation (Brown et al., 2003; Rauscher et al., 2012), Fenton's Reagent (Flotron et al., 2005; Jonsson et al., 2006; Pardo et al., 2015a; Venny et al., 2012), ozonation (Jonsson et al., 2006; Luster-Teasley et al., 2009; Rivas et al., 2009) and activated persulfate (PS) (Killian et al., 2007; Liang and Guo, 2010; Zhao et al., 2013). Particularly, in the last ten years, the application of activated PS has been of increasing relevance, as it has several advantages, such as the high oxidation potential of the sulfate radicals (E = 2.60 V), its higher stability in soil at room temperature than hydrogen peroxide or ozone, its high solubility and the fact that it is a cost-effective technique which makes it an attractive alternative to traditional ISCO methods, such as Fenton's reagent, permanganate or ozonation (Tsitonaki et al., 2010). On its own, PS ion (E = 2.05 V) has a lower oxidation potential than sulfate radicals, thus being less effective to degrade recalcitrant compounds. In aqueous solution, PS salts dissociate into PS anions, which act as electrophilic specie, generating sulfate anions (Eqs. (1) and (2)):

$$Na_2S_2O_8 \rightarrow 2Na^+ + S_2O_8^{2-} \quad (1)$$

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \quad (2)$$

To enhance the effectiveness of PS, some activators can be used for the production of sulfate radicals, therefore activation can be achieved via Fe^{2+} (Eq. (3)) by adding ferrous salts or zerovalent iron (Eq. (4)) (Chen et al., 2015; Killian et al., 2007; Peluffo et al., 2015), by heat or light activation, by peroxide activation (Zhao et al., 2013), or more recently by alkaline activation (Deng et al., 2014; Liang and Guo, 2012; Liang and Lei, 2015). In addition, during PS activation, sulfate radicals and hydroxyl radicals (E = 2.70 V) may coexist, as shown in Eqs. (5) and (6) (Al-Shamsi and Thomson, 2013b). Activation pathways from Fe^{3+} may occur if Fe^{3+} is reduced to Fe^{2+}, being this step promoted by the presence of certain species, which can act as electron transfer species, like quinone type compounds (Chen and Pignatello, 1997; Rodriguez et al., 2014), which can be found as oxidation intermediates during the treatment, or as certain components present in the humic acids in soil (Fukushima and Tatsumi, 1999; Kappler et al., 2004).

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\cdot-} \quad (3)$$

$$Fe^0 + S_2O_8^{2-} \rightarrow Fe^{2+} + SO_4^{2-} \quad (4)$$

$$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot} \quad (5)$$

$$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + OH^{\cdot} + H^+ \quad (6)$$

On the other hand, an important drawback that should be taken into account is the fact that Fe^{2+} can act as radical scavenger of the sulfate radicals, producing a non-productive consumption of the oxidant (Eq. (7)) (Liang et al., 2004; Romero et al., 2010; Vicente et al., 2011):

$$SO_4^{\cdot-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \quad (7)$$

To minimize reaction in Eq. (7), a slow release of Fe^{2+} to the media has been proposed (Vicente et al., 2011), which can be also achieved by using zerovalent iron (ZVI) (Rodriguez et al., 2014). Indeed, it has been reported higher removal efficiencies of pollutants when activation was due to ZVI, either in the form of granular, micro or nanoparticles, than Fe^{2+} (Oh and Shin, 2014; Pardo et al., 2015b; Rodriguez et al., 2014). Despite the benefits of ZVI, the difficulties derived from the injection of granular particles or powder, which make its application unsuitable, have led to the development of nanoparticles of zerovalent iron or nanoscale particles of zerovalent iron (nZVI). In this regard, injection of nZVI in the subsurface would solve the problems related to the injection of higher size particles (Al-Shamsi and Thomson, 2013b). Given the reactivity due to its reducing potential, it has been reported the effectiveness of nZVI as reducing agent for certain pollutants, like chlorinated hydrocarbons (Kober et al., 2014; Kocur et al., 2014), as well as an efficient PS activator for the degradation of aliphatic hydrocarbons (e.g. Diesel) or PAH (Pardo et al., 2015b; Peluffo et al., 2015). In accordance to literature, the vast majority of the studies that have assessed the use of activated PS for the remediation of hydrocarbon contaminated

soils have been carried out from batch experiments. However, there is an evident lack of research regarding the study of the remediation of hydrocarbon contaminated soils in column conditions (Lemaire et al., 2013; Usman et al., 2013). Since column studies represent a better approach to field scale application than batch experiments, they provide more accurate data for its real development. Therefore, the aim of this work is focused on the study of the effectiveness of activated PS by Fe^{3+} and nZVI in the remediation of a contaminated soil with Phenanthrene (PHE), Anthracene (ANT), Pyrene (PYR) and Benzo(a)pyrene (BaP), artificially spiked and aged for three months. Runs have been carried out in column by using a flow rate close to the hydraulic conductivity of the soil tested. In addition, during the 25 days remediation process, oxidant concentration, iron in solution and pH were monitored. Finally, after treatment, soil was taken at different column lengths and profiles of remaining iron and PAHs were analysed.

2. Materials and methods

2.1. Reagents

PHE ≥99.5% (sublimed grade), ref. 695114, from Aldrich (France), ANT 99% (ReagentPlus), ref. 141062, from Aldrich (France), PYR 98%, ref. 185515, from Aldrich (France) and BaP ≥96%, ref. B1760, from Sigma (France) were used for soil spiking and HPLC analysis in order to quantify their concentration in the soil after extraction. 9-10, Anthraquinone (ATQ) 97%, ref. A90004 was used for calibration and quantification. Sodium PS ≥98%, used as oxidant, was purchased from Sigma-Aldrich; ferric sulfate from Panreac 75% (anhydrous basis); and air-stable nZVI powder (NANOFER STAR) from Nanoiron s.r.o. were used, respectively, as activator species. Ethylenediaminetetraacetic acid (EDTA) tetrasodium salt dihydrate ≥98% was used as chelating agent for the extraction of iron labile pool of the soil samples. Regarding PS analysis, sodium hydrogen carbonate 99.7% (Panreac), potassium iodide >99.5% (Fisher Chemical) and sodium thiosulfate pentahydrate 99.5% (Sigma-Aldrich) were employed. Sodium thiosulfate was also employed to quench PS. Sodium sulfate anhydrous 99%, from Fisher Chemical, Acetone 99.8% HPLC gradient grade from Fisher Chemical and n-hexane 99% HPLC grade from Scharlab were used for the extraction of contaminants in soil. Phosphoric acid ≥85% from Sigma-Aldrich and Acetonitrile HPLC gradient grade from Fisher Chemical were both used as mobile phase in HPLC for PAH analysis. Nitric acid 69.5% was employed for the stabilization of iron ions for metal determination in aqueous solution by MP-AES analysis.

2.2. Soil spiking and aging with PAHs

The soil selected for this study was categorized as sandy clay loam BT horizon (pH = 7.22; total organic carbon = 0.196%, free iron oxides = 7235 mg kg^{-1}, dp < 2 mm, hydraulic conductivity = 14.1 cm day^{-1}) from the Autonomous Community of Madrid. Soil properties and the characterization procedure, except the determination of the hydraulic conductivity, are detailed in previous works (Pardo et al., 2014; Vicente et al., 2012). Soil spiking was carried out as reported elsewhere (Kulik et al., 2006; Mora et al., 2014; Peluffo et al., 2015), spreading slowly an acetone stock solution of the contaminants to the clean soil, being mixed manually with a spatula simultaneously. After spiking, contaminated soil was kept at room temperature in the absence of light for three months in order to ensure a certain grade of aging. As a result, initial concentrations of each PAH in the spiked soil ranged between 105 and 140 $mg_{PAH}\ kg^{-1}{}_{dry\ soil}$.

2.3. Experiments in column

Runs were performed in glass columns of 24.6 cm length and 3 cm internal diameter, each column was filled and compacted with near 150 g of soil, with a length of 17.5 cm. In order to avoid channelling, packed glass beads were placed to a length of 1.5 cm below and above the soil bed. Bulk density of the dried porous soil bed was 1.445 ± 0.012 g cm^{-3}, inlet flow was fed by a peristaltic pump at 43.2 ± 1.5 cm^3 day^{-1}, corresponding to an interstitial velocity of 13.9 cm day^{-1} in the column, which was close to the flow velocity of groundwater in saturation conditions (14.1 cm day^{-1}). Prior to each run, dry columns were filled, from bottom to top, with Milli-Q water at the selected inlet flow in order to reach saturation conditions. Pore volume of soil column was 74 ± 0.5 cm^3. Properties of the columns and a scheme of the experimental setup are shown in the Supplementary Material (Table TS1 in the online version at http://dx.doi.org/10.1016/j.scitotenv.2016.04.197., Figs. FS1 in the online version at http://dx.doi.org/10.1016/j.scitotenv.2016.04.197. and FS2 in the online version at http://dx.doi.org/10.1016/j.scitotenv.2016.04.197., respectively).

2.4. Oxidation runs and sampling

Remediation runs were conducted under the following conditions:

- Blank: Milli-Q water was added during 25 days.
- Control: To analyze the contribution of iron naturally present in the soil. An aqueous solution of 0.2 mmol cm^{-3} PS, without iron addition, was injected for 25 days.
- CPS1: Two aqueous solutions, one containing 0.2 mmol cm^{-3} (200 mM) PS and other containing 0.0558 mg cm^{-3} (1 mM) Fe^{3+} in Ferric sulfate, were simultaneously fed for 25 days.
- CPS2: In order to introduce a similar quantity of iron in the column than in CPS1, an aqueous suspension 0.0558 mg cm^{-3} (1 mM) nZVI was fed into the column for 25 days at 43.2 cm^{-3} day^{-1}. Afterwards (zero time), an aqueous solution 0.2 mmol cm^{-3} (200 mM) PS was fed for 25 days.
- CPS3: An aqueous suspension 50 mg cm^{-3} (900 mM) nZVI was fed for 1 day. Subsequently (zero time), a 0.2 mmol cm^{-3} (200 mM) PS solution was added for 25 days.

PS in all runs and Fe concentration in runs CPS1 and CPS2 were selected in accordance with a previous work, based on experiments performed in batch mode (Peluffo et al., 2015). Iron concentration in run CPS3 was selected for studying the influence of the amount of nZVI injected on the removal efficiency of the contaminants. Sequence of injection was based on its suitability for real applications, in case of CPS1, Fe^{3+} was injected simultaneously to PS as they do not react immediately, since Fe^{3+} needs to be reduced firstly to Fe^{2+} for PS activation. In CPS2, nZVI were firstly injected to create an activation zone in the column prior to PS addition. Indeed, this mechanism has been tested to be effective for the removal of a TCE-contaminated soil (Al-Shamsi and Thomson, 2013a).

Moreover, to ensure an optimal homogenization of the suspension and to minimize nZVI corrosion, nitrogen (technical grade) was bubbled up during nZVI injection, from bottom to top through the suspension.

Therefore, a summary of the experiments carried out and their corresponding operation conditions is shown in Table 1.

During the 25-day treatments, samples were withdrawn periodically at the column exit and the effluent from the column was continuously collected in volumes ranging from 15 to 70 cm^3. PS concentration was analysed by potentiometric titration, and total iron was determined in solution either by Atomic Emission Spectrometry induced by Microwave Plasma (MP-AES) or by colorimetry. Furthermore, in order to verify the presence of PAH eluted in the aqueous effluent collected, a liquid-liquid extraction was performed by adding 15 cm^3 of hexane to the aqueous volumes collected and stirred for 4 h; the organic extract was analysed by HPLC to quantify the PAHs, as explained in the analysis section. Replicate analyses of the effluents were performed in duplicate, showing their corresponding results as average values with a relative standard deviation (RSD) lower than 10% for PS, iron concentration and pH.

Table 1
Experimental conditions of the remediation runs. Q = 43.2 cm^3 day^{-1}. T = 25 °C.

	C_{PS0} (mmol·cm^{-3})	C_{Fe0} (mg·cm^{-3})	Fe type	Injection	Remediation time (days)
Blank	0	0	–	Water	
Control	0.2	0	–	PS only	
CPS1	0.2	0.0558	Fe^{3+}	PS + Fe^{3+} simultaneously	
CPS2	0.2	0.0558	nZVI	1st stage. nZVI inyection (25 days) 2nd stage. PS inyection (25 days)	25
CPS3	0.2	50	nZVI	1st stage. nZVI inyection (1 day) 2nd stage. PS inyection (25 days)	

After each treatment, soil was removed from the glass column and divided into 4 sections of similar weight of wet soil (ranging from 52 to 55 g); located at different column lengths. From each section, about 40 g of wet soil were mixed with 15 mL of 400 mM thiosulfate, a quenching agent for hydroxyl and sulfate radicals, and stored under low temperature (≤4 °C) until the application of microwave assisted solvent extraction. The remaining 10 g of wet soil were dried at 105 °C for 1 h to determine the water content. The resulting dried soil was used to carry out, by triplicate, the extraction of iron labile fraction, where 2 g of dried soil were stirred with 20 cm^3 of 50 mM EDTA for one hour (Quevauviller, 1998) and iron in solution was analysed by colorimetry. The natural content of labile iron in the non-treated soil was also determined, which was 32 mg_{Fe} $kg^{-1}{}_{drysoil}$, similar to the value of 40 mg_{Fe} $kg^{-1}{}_{drysoil}$ obtained by (Vicente et al., 2012) after extraction with sodium citrate. Therefore, the difference between labelled iron obtained by EDTA extraction, after and before treatment, represented the amount of labile iron retained by external addition (sorbed or precipitated) in the soil during remediation.

Besides, since iron could also be retained around the glass spheres placed below the soil section, its content was determined by acid digestion of the beads with HNO_3 (50% *v*/v) and stirring for 3 h at 60 °C; finally, after filtration of the aqueous phase, iron content was analysed by MP-AES.

The PAHs content in each soil section, after the remediation treatments, was determined following the EPA method 3546 procedures, based on the use of microwave extraction from solid contaminated matrix, where the remaining fraction of wet soil, previously quenched, was mixed with anhydrous sodium sulfate and crushed in a ceramic mortar, obtaining a dry powder. PAHs extractions and analyses were carried out by triplicate, through the addition of 10 g of dry powder with 25 cm^3 of a mixture of hexane:acetone 1:1. For the extraction procedure, a microwave extraction device was used (Milestone Ethos One), carrying out the extraction for 30 min at 110 °C; consisting of an initial ramp of 15 min from room temperature to 110 °C, then holding 110 °C for 15 min, under a maximum power applied of 1000 W.

2.5. Analysis

Analysis of PS and iron concentration, pH measurement and PAH determination, are reported elsewhere (Peluffo et al., 2015). Nevertheless, given the interferences during MP-AES analysis of some samples with high concentration of sodium, the analysis of iron in solution was performed using a DR/890 colorimeter (HACH), by mixing 10 cm^3 of aqueous solution with Ferrover® Iron reagent, based on the ability of 1.10-Phenanthroline-*p*-toluenesulfonic acid salt to selectively complex iron ions.

3. Results and discussion

3.1. Natural attenuation of PAHs

Prior to the treatments, concentrations of PAHs in soil were analysed one day (freshly spiked) and three months after spiking: ANT (104.6 ± 3.6 mg kg^{-1} freshly spiked and 5.75 ± 0.39 mg kg^{-1} after aging), ATQ (0 mg kg^{-1} freshly spiked and 97.7 ± 5.9 mg kg^{-1} after aging), PHE (139.2 ± 5.1 mg kg^{-1} freshly spiked and 137.7 ± 7.3 mg kg^{-1} after aging), PYR (130.1 ± 6.0 mg kg^{-1} freshly spiked and 125.5 ± 3.4 mg kg^{-1} after aging), BaP (111.4 ± 7.8 mg kg^{-1} freshly spiked and 112.9 ± 4.4 mg kg^{-1} after aging).

It was observed during the three months period of soil aging that 96% of the initial ANT was naturally degraded to ATQ, via abiotic or biotic processes. The abiotic processes are commonly due to the role of some metals, present in the structure of clay minerals such as Fe, Cu, Al, Mg, among others, which, as interchangeable cations, may promote the transformation of ANT to ATQ (Li et al., 2015; Soma and Soma, 1989). On the other hand, these abiotic processes may occur simultaneously to biotic phenomena by the presence of some soil microorganisms (fungi or bacteria), capable of degrading the contaminants (Field et al., 1992; Li et al., 2014, 2015). With respect to the other pollutants in soil, no significant changes in concentrations of PHE, PYR or BaP were noticed.

3.2. Iron profile, PS profile and iron distribution

Analysis of profiles of PS, pH an iron concentration is detailed in this part, as well as the distribution of iron retained in the different sections of the column from the extraction of labile iron with EDTA.

3.2.1. Iron profile

Results corresponding to run CPS1 are given in Fig. 1. Profile of iron concentration in the effluent is shown in Fig. 1a. In this figure the total amount of iron retained in the column, $q_{Fe\ col}$ (average value calculated by Eq. (8)) and the fraction of the iron introduced in the column that has been retained in the soil (% Fe retained, calculated by Eq. (9)) are also plotted.

$$q_{Fe\,col}\left(\frac{\text{mg}}{\text{cm}^3_{column}}\right) = \frac{Q}{V_{column}}\int_{t_{inj}}^{t}(C_{Feo} - C_{Fe})dt \tag{8}$$

$$\%_{Fe\ retained} = \frac{q_{Fe\,col}}{\frac{C_{Fe0}\cdot V_{injected}}{V_{column}}}\cdot 100 \tag{9}$$

C_{Feo} and C_{Fe} correspond to the iron concentration in the column at the beginning and at the exit of the column, respectively, V_{column} is the volume of the column (173 cm^3), Q is the total flow fed to the column (43.2 cm^3 day^{-1}), t_{inj} corresponds to the time when the iron began to be injected (days) and $V_{injected}$ is the total volume of Fe^{3+} solution or nZVI suspension fed into the column.

PS concentration and pH at the exit are given in Fig. 1b. The amount of PS reacted in the column, expressed as an average value of moles of PS consumed by kg of soil and day, ($N_{PS\ consumed}$), were calculated from the PS mass balance, according to Eq. (10) (applicable at time > t_{delay} = 1.72 days).

$$N_{PS\ consumed}\left(\frac{\text{mg}}{\text{kg soil}\cdot\text{day}}\right) = \frac{Q}{W\ soil}(C_{PS0} - C_{PS}) \tag{10}$$

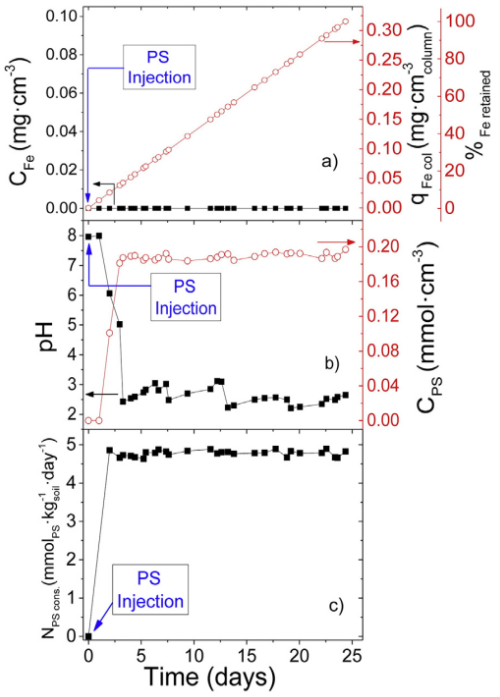

Fig. 1. Experiment CPS1, profiles of iron concentration at the exit (black)t and accumulated (red) (3a); pH (black) and PS (red) at the exit (3b) and $N_{PS\ consumed}$ (3c). $[PS]_0 = 0.2$ mmol cm^{-3}, $[Fe^{3+}]_0 = 0.0558$ mg cm^{-3}, $T = 25$ °C (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

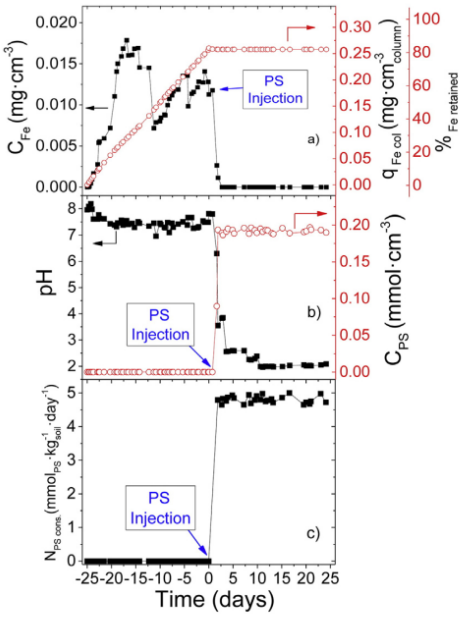

Fig. 2. Experiment CPS2, profiles of iron concentration at the exit (black) and accumulated (red) (4a); pH (black) and PS (red) at the exit (4b) and $N_{PS\ consumed}$ soil (outlet-inlet) (4c). $[PS]_0 = 0.2$ mmol cm^{-3}; $[nZVI]_0 = 0.0558$ mg cm^{-3}, $T = 25$ °C (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Being C_{PS0} and C_{PS} the PS concentrations at the column inlet and outlet, respectively. Profile of $N_{PS\ consumed}$ is shown in Fig. 1c.

In Figs. 2 and 3, the corresponding results obtained in CPS2 and CPS3, respectively, are given. In these runs, zero time was also considered as the time when PS was fed into the column.

As can be seen in Fig. 1a and b (CPS1), despite the acidic pH (around 2), iron concentration in the column effluent was negligible. On the other hand, in run CPS2, although injection protocol was different than in CPS1, the amount of iron injected was similar. In this context, iron concentration in the column effluent ranged from 0 to near 0.018 mg cm^{-3} (18 mg L^{-1}) during the 25 days prior to PS injection, to consequently drop to near zero after the oxidant addition (Fig. 2a). In run CPS3, no iron was detected in the effluent during the period when nZVI was injected (1 day). Nevertheless, after PS addition, in run CPS3, a sharp increase of Fe concentration, up to 4 mg cm^{-3} (4000 mg L^{-1}), was noticed at the exit of the column, that progressively decreased until the end of treatment (Fig. 3a). In this sense, the increase of Fe concentration in the effluent could be due to the oxidation of nZVI to Fe^{2+}, and subsequently to Fe^{3+}.

3.2.2. PS consumption

Regarding PS and pH profiles, it was noticed a similar trend in runs CPS1 (Fig. 1b) and CPS2 (Fig. 2b), where a sharp drop of pH as well as a fast increase in PS concentration in the effluent occurred after PS addition. In addition, in both runs pH reached a steady value close to 2 and a PS concentration near 0.2 mmol cm^{-3} after about 1.7 days, being this time in agreement with that corresponding to the calculated residence time for the pore volume of the column (1.72 days). On the other hand, although a similar trend was observed for run CPS3, steady values for pH (near 2) and PS concentration (~0.2 mmol cm^{-3}) were reached at about 23 days after PS injection (Fig. 3b). Accordingly, given that PS

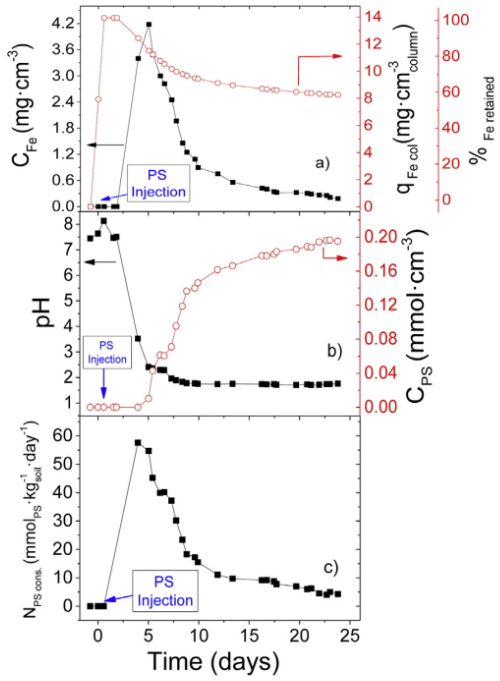

Fig. 3. Experiment CPS3, profiles of Iron concentration at the exit (black) and accumulated (red) (5a); pH (black) and PS at the exit (red) (5b) and N_{PS} consumed (5c). $[PS]_0 = 0.2$ mmol cm^3; $[nZVI]_0 = 50$ mg cm^{-3}, $T = 25$ °C (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

consumption was higher in CPS3 than in CP1 or CPS2 (Figs. 1c, 2c and 3c) this time delay was much higher than that corresponding to the 1.72 days of residence time of pore volume. This can be explained due to the fact that a much higher concentration of iron in column was present in CPS3 than in CPS2 or CPS1 (Figs. 3a, 2a and 1a, respectively).

Specifically, in terms of PS consumption, in runs CPS1 and CPS2, the amount of PS reacted in the column during 25 days was about 4.6–5.0 mmol kg^{-1}_{soil} day^{-1}, while in CPS3, the maximum PS reacted was about 60 mg kg^{-1}_{soil} day^{-1}, which was reached at about five days since injection, matching as well with the maximum iron concentration in the effluent (Fig. 3a). An important consequence related to the sharp decrease in pH in all runs may be attributed to the depletion of the soil buffer capacity due to the PS fed to the column. In this sense, this effect may result in important modifications of metal mobility, as well as can change the behavior of the mechanisms involving the oxidation of contaminants (Siegrist et al., 2011).

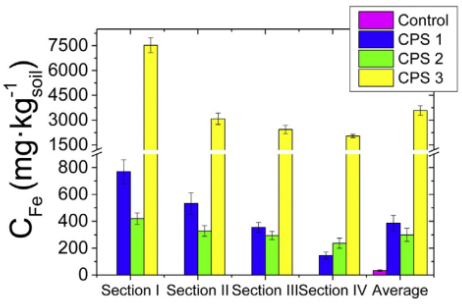

Fig. 4. Distribution of labile iron in the soil column after 25 days of treatment with PS. Fe labile naturally present in soil before PS addition = 4.8 mg (referred to the 150 g of soil in the column).

3.2.3. Iron distribution

According to Fig. FS3 in the supplementary material, which shows photographs of the columns at two moments, firstly when PS began to be injected and after the 25-day treatment, it was observed that part of the nZVI were retained between the glass beads located below the soil column before PS was injected (CPS2 and CPS3). Nevertheless, it was noticed, after treatment, that in run CPS2 all nZVI were transported progressively along the soil column, while in run CPS3 a remarkable amount of nZVI (66.7% of the iron retained in the column) still remained in the glass beads. As well as this fact was confirmed visually, as shown in Fig. FS3, the results in Table 2, which shows the distribution of iron (mg) in the column and in the glass beads, confirmed that near a 40% of the nZVI initially injected in CPS3 did not pass through the soil.

In runs CPS1 and CPS2, where no iron was detected after acid digestion of the glass beads, total iron extracted with EDTA in all soil fractions was quite similar (59.4 mg in CPS1 and 46.7 in CPS2) as well as it matched accurately to the iron introduced into the column, calculated as $q_{Fe} \cdot V_{column}$.

Besides, it is noteworthy to point out that the amount of Fe labile naturally present in soil before PS addition was 4.77 mg (referred to the 150 g of soil in the column), being remarkably lower than the labile iron extracted after all treatments.

With regard to the distribution of labile iron present in each of the four different sections in the soil column after treatment, which is shown in Fig. 4, it was noticed a progressive decrease on labile iron concentration along the column. However, in run CPS1, higher differences in the Fe profile with column length were noticed, suggesting that nZVI particles were not as strongly sorbed by the soil in CPS2 and CPS3 as it was Fe^{3+} in CPS1.

Furthermore, although an important fraction from the nZVI injected was retained in the glass beads in CP3, the total amount of nZVI in soil in run CPS3 was remarkably higher than that found in runs CPS1 and CPS2.

Table 2
Iron in column after 25 days of treatment with PS.

		CPS1	CPS2	CPS3
Total iron fed to the column (mg)		54.8	56.5	2422
Total iron eluted from the columnt (mg)		0	11.7	987
		(0%)	(20.7%)	(40.8%)
Total Fe retained in column (% $Fe_{retained}$)		54.8	44.8	1435
		(100%)	(79.2%)	(59.2%)
Fe distribution in column	In Spheres (by acid digestion) mg % of iron retained in column	0	0	960
		0%	0%	(66.7%)
	Extracted from soil by EDTA (mg) % of iron retained in column	59.4	46.7	546
		(100%)	(100%)	(33.3%)
Labile Fe natural in soil (mg)		4.8		

3.3. PAHs removal efficiencies

From the analysis of the effluent withdrawn in the control run, as well as in the oxidation runs, negligible amount of PAH_s (<1% of the total concentration of PAHs) were detected after extraction with hexane.

The remaining concentrations of each PAH at each soil section of the column (CPS1, CPS2 and CPS3), as well as the average concentrations in the whole column (control, CPS1, CPS2 and CPS3) are shown in Fig. 5. Furthermore, since ANT was naturally degraded (>95%) to ATQ, the profile of ATQ is shown instead of that corresponding to ANT.

As can be seen in Fig. 5, removal efficiencies of the different PAHs followed the order BaP > PYR > PHE > ATQ, which is in agreement with previous works based on batch studies (Pardo et al., 2015a; Peluffo et al., 2015). In this sense, this trend is also explained by the importance of the structure-related reactivity, where the ionization potential (−Ip), as an approximation of the energy of the highest occupied molecular orbital (HOMO), provides an accurate approximation of their reactivity towards chemical oxidation (Jonsson et al., 2007; Kitti et al., 2003), mainly when sorption phenomena are not substantial enough due to the short period of aging and the low organic matter content in soil. Therefore, according to literature (Murov et al., 1993), the different ionization potentials followed the same order than the removal efficiencies achieved, being BaP (−7.12 eV) > PYR (−7.41 eV) > PHE (−7.86 eV) > ATQ (−9.25 eV). Indeed, ATQ high stability has been already reported and commented in literature (Forsey et al., 2010; Peluffo et al., 2015), thus higher contact time with the oxidant would be needed to improve its abatement.

Regarding BaP, its removal efficiencies were practically 100% in all runs and all sections, while for the rest of PAHs, the highest removal efficiencies were found in section I (bottom of soil column) and the lowest corresponded at the column exit (section IV). This fact can be related to the Fe profiles along the soil column (Fig. 4), finding a higher iron content in soil with a higher removal efficiency of PAHs. In fact, the lowest PAHs removal efficiencies reached corresponded to the control run (7%, 7%, 58%, 96% removal for PHE, ATQ, PYR and BaP, respectively). Therefore, it is noticeable that, without external addition of iron, persulfate alone could be able to oxidize BaP almost completely and PYR up to a certain extent. Instead, PHE and ATQ were slightly abated, confirming that external addition of iron increased the effectiveness of the remediation technique.

Furthermore, despite the similar amount of labile iron in soil obtained in CPS1 (Fe^{3+}) and CPS2 (nZVI), higher PHE and PYR removal efficiencies were achieved in CPS2 (nZVI). PAHs removal in run CPS3 was higher than in CPS2, but differences were lower than expected given that the amount of labile iron in CPS3 was much higher.

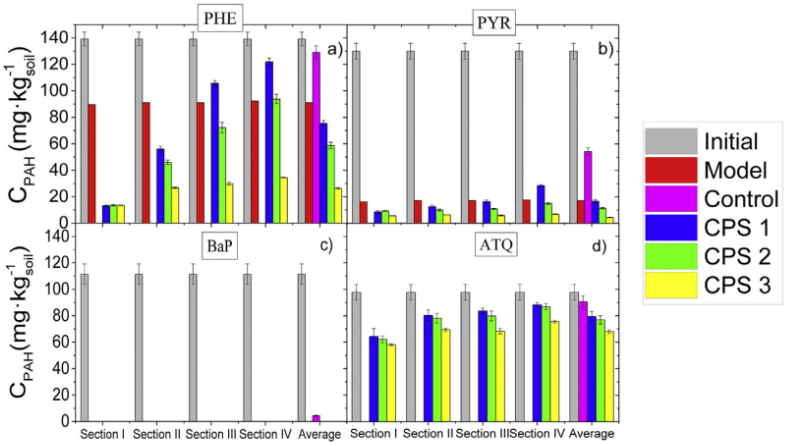

Fig. 5. Remaining concentrations of the PAHs at different sections of the column after 25 days of treatment. a) PHE, b) PYR, c) BaP and d) ATQ. (Runs in Table 1) Soil Length 17.5 cm, interstitial velocity (13.9 cm·day^{-1}).

According to this, a significant non-productive PS consumption may have occurred in CPS3 (Eq. (7)). With regard to ATQ removal, only a 40% of ATQ was abated under the strongest conditions (nZVI 50 mg cm^{-3}).

3.4. Comparison with results obtained in batch

For the scope of comparison, the kinetic information obtained elsewhere from batch experiments under the same oxidant and activator concentrations (Peluffo et al., 2015) has been used to predict the average PS consumption and PAHs removal efficiencies in the soil column. In this sense, assuming that PAHs concentration in the aqueou phase was negligible, the removal rate of PAHj at each column length z can be described by Eq. (11)

$$\frac{-dC_{PAH}}{dt} = k_{wj} \cdot C_{PAH_j} \tag{11}$$

Being k_{wj} the apparent kinetic constant of oxidation of each contaminant (day^{-1}) and C_{PAH} the pollutant concentration in soil (mg kg$^{-1}{}_{soil}$).

On the other hand, PS at the column exit can be calculated by the following expression:

$$C_{PS} = C_{PS0} e^{-k_{wPS} \cdot \rho_L \cdot L / u_i} \tag{12}$$

Where k_{wPS} is the apparent kinetic constant for PS consumption (L kg^{-1} day^{-1}), C_{PS} PS concentration in the effluent (mmol L^{-1}), ρ_L the bulk density of the soil column (1.445 kg L^{-1}), L the soil height (0.175 m) and u_i the interstitial velocity (0.14 m day^{-1}).

Values of the kinetic constants for Eqs. (11) and (12) were obtained in batch assuming C_{PS} = 0.2 mmol cm^{-3} (200 mM) and C_{Fe3+} = 0.0558 mg cm^{-3} (1 mM) (Peluffo et al., 2015). Thus, $k_w^{PHE} = 1.69 \cdot 10^{-2}$ (day^{-1}), $k_w^{PYR} = 8.15 \cdot 10^{-2}$ (day^{-1}), $k_w^{BaP} = 5.48 \cdot 10^{-1}$ (day^{-1}), $k_{wPS} = 2.5 \cdot 10^{-2}$ (L kg^{-1} day^{-1-1}).

After the delay time (1.72 days), PS concentration at the exit of the soil column was predicted by integrating Eq. (12) with the kinetic constant, corresponding to PS, ($2.5 \cdot 10^{-2}$ L kg^{-1}·day^{-1}). In this regard, predicted PS concentration at the exit of the soil column was about 0.194 mmol cm^{-3} (194 mM), being similar to the value obtained experimentally in the effluent. Therefore, given that PS conversion along the column was low, PS concentration could be considered constant with the column length.

On the other hand, conversion of BaP, PHE and PYR (X_{PAHj}, Eq. (13)) with time were predicted (Fig. 6) by Eq. (14) from the integration of Eq. (11), assuming, C_{PS} = 200 mM, C_{FeIII} = 1 mM and taking the values of k_w corresponding to the PAHs.

$$X_{PAH_j} = \frac{C_{PAH_{j0}} - C_{PAH_j}}{C_{PAH_{j0}}} \tag{13}$$

$$1 - X_{PAH_j} = e^{-k_{wj}t} \tag{14}$$

Accordingly, it is noteworthy that it was not considered an iron profile along the soil column in Eq. (14), thus the PAHs conversions estimated in Fig. 6 are expressed as an average value along the column. As a result, predicted values of PAHs concentration, at 25 days of treatment, were 89.8 mg kg^{-1} of PHE, 16.3 mg kg^{-1} of PYR and almost 0 mg kg^{-1} of BaP. These estimated values, which are included as blue bars in Fig. 5, can be compared to the average PAHs concentrations in the column in run CPS1, obtaining a good match for the overall removal efficiencies, but losing accuracy if the estimated values are compared to those obtained for each section.

4. Conclusions

It has been studied the effectiveness of activated PS for the remediation of a PAH contaminated soil, aged for three months, in column experiments. Fe^{3+} and nZVI were used as PS activators, achieving almost total removal of BaP and finding that PHE was the most recalcitrant pollutant, being also in accordance with the results obtained in batch from

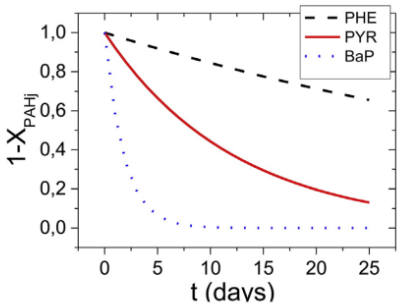

Fig. 6. Conversion of each PAH in the soil column with time predicted by Eq. (14). A solution 0.2 mmol cm^{-3} (200 mM) PS and 0.0558 mg cm^{-3} (1 mM) Fe^{3+} is fed to the soil column.

a previous work (Peluffo et al., 2015). As it was noticed, as well as it happened in batch runs, higher efficiencies were reached using nZVI than Fe^{3+} under similar amounts of iron injected. Besides, in spite of the acidic pH, Fe^{3+} injected was more strongly retained in the soil column than nZVI particles, being higher the concentration at the column entrance. On the other hand, as a consequence of nZVI injection, a smoother profile of Fe along the column was observed.

Regarding iron retained in the soil, it was calculated from the mass balance between iron in the effluent at the exit of the column and in the entrance, being this type of iron identified as labile type.

With respect to the removal efficiencies of PAHs, the highest conversions were found in the nearer sections to the injection source, thus being related as well with the iron profile found along the column.

From the monitoring of the effluents withdrawn during treatment, it was observed that PS overtook quickly the buffer capacity of the soil and pH dropped sharply in all runs. Moreover, a low consumption of PS was found, being about 4.9 $mmol_{PS}\ kg^{-1}\ day^{-1}$ for runs where the lower concentration of iron was used, but it reached a value near 60 $mmol_{PS}\ kg^{-1}\ day^{-1}$ when nZVI was added at the highest concentration, corresponding to a non-productive PS consumption with a small improvement in PAHs removal.

In conclusion, all the information provided in this work suggests the suitability of injection of nZVI, as it offered the best results, prior to PS injection for the remediation of PAHs-contaminated soils. Nevertheless, further research, regarding studies under flow conditions, should be needed in order to widen the knowledge in the subject and to optimize the remediation conditions.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2016.04.197.

Acknowledgements

The authors acknowledge the financial support from the Comunidad Autonoma de Madrid provided through the project CARESOIL (S2013-MAE-2739) and from the Spanish Ministry of Economy and Competitiveness, grant BES2011-044329 and project CTM2013-43794-R.

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5.

CONCLUSIONES/ *CONCLUSIONS*

CONCLUSIONES

De los resultados obtenidos en la remediación de un suelo contaminado con compuestos orgánicos (etilbenceno, fueloil –biodiesel- o PAHs), poco solubles en fase acuosa y poco biodegradables mediante la aplicación de oxidación química con peróxido de hidrógeno y persulfato, con hierro como activador y adición o no de agente quelante, se han podido extraer las siguientes conclusiones:

1. **Eliminación de etilbenceno:**

   1.1. Dado que la degradación del contaminante transcurre en la fase acuosa, la conversión de etilbenceno se encuentra limitada por su solubilidad en dicha fase (C_{EB}^{*}), 180 mg·L^{-1}, y al mismo tiempo depende inversamente de la concentración inicial de etilbenceno en el suelo (C_{EB0}), como se indica en la Ec. [5.1].

$$X_{EB} = \frac{k \cdot C_{H_2O_2}^{n} \cdot C_{EB}^{*} \cdot t}{C_{EB_0}} \cdot \frac{V_L}{W_{suelo}} \qquad [5.1]$$

   1.2. El reactivo Fenton modificado con citrato de sodio como agente quelante (C_{CT0} = 50 mmol·L^{-1} en fase acuosa) permite prolongar el tiempo de vida del oxidante y mantener el hierro en disolución a un pH cercano a la neutralidad. En las condiciones experimentales usadas se consiguieron eficiencias de eliminación cercanas a la totalidad hasta una concentración de etilbenceno en suelo de 6600 mg·kg^{-1}. Para los tratamientos con 20000 mg·kg^{-1} (188 mmol·kg^{-1}) de etilbenceno en suelo, la máxima conversión de etilbenceno alcanzada fue de un 60% (C_{CT0} = 50 mmol·L^{-1}, $C_{H_2O_20}$ = 4410 mmol·L^{-1}, $C_{Fe(III)0}$ = 5 mmol·L^{-1})

   1.3. La presencia de suelo en el medio facilita la transferencia entre las fases acuosa y orgánica. La oxidación de etilbenceno fue más rápida cuando la reacción se llevó a cabo en presencia de suelo que en fase líquida. Sin embargo, no se observaron diferencias significativas en la conversión final de etilbenceno, siendo X_{EB} = 98% (C_{CT0} = 50 mmol·L^{-1}, $C_{Fe(III)0}$ = 27 mmol·L^{-1}, $C_{H_2O_20}$ = 1470 mmol·L^{-1}, N_{EB0} = 0.094 mmol) y X_{EB} = 60% (C_{CT0} = 50

mmol·L^{-1}, $C_{Fe(III)0}$ = 5 mmol·L^{-1}, $C_{H_2O_20}$ = 4410 mmol·L^{-1}, N_{EB0} = 0.94 mmol), alcanzadas en 72 horas, cuando el tratamiento se realizó en suelo contaminado y X_{EB} = 96% y X_{EB} = 59 %, respectivamente , alcanzados en 144h horas aproximadamente, cuando la reacción fue únicamente en fase líquida. Sin embargo, la presencia de suelo también aumenta el consumo improductivo de peróxido de hidrógeno, haciendo que éste también se consuma más rápidamente cuando la reacción transcurre en presencia de suelo.

2. **Eliminación de biodiesel B20:**

2.1. Como consecuencia de la menor solubilidad de los componentes de una mezcla de 80% de hidrocarburos de petrodiesel y 20% de ésteres metílicos de ácidos grasos, con respecto a la del etilbenceno, durante la aplicación del reactivo Fenton modificado en las condiciones más favorables (C_{CT0} = 50 mmol·L^{-1}, $C_{Fe(III)0}$ = 20 mmol·L^{-1}, $C_{H_2O_20}$ = 4000 mmol·L^{-1}), la máxima conversión de contaminante alcanzada no superó un 37%.

2.2. La aplicación del reactivo Fenton-like para la eliminación de biodiesel B20, a través de la adición de peróxido de hidrógeno en exceso y Fe(III) en forma de sulfato férrico, ofreció los mejores resultados en términos de eficiencia de eliminación (X_{TPH} ~ 75%) para una concentración de 1000 mg·kg^{-1} del contaminante en suelo, donde en apenas dos horas se produjo el consumo casi total del oxidante (~90%) ($C_{Fe(III)0}$ = 20 mmol·L^{-1}, $C_{H_2O_20}$ = 4000 mmol·L^{-1}). A pesar de haberse obtenido una alta eliminación del contaminante, la vida del oxidante en las condiciones utilizadas era corta, lo que obligaría a reducir la distancia entre los puntos de inyección en un tratamiento in situ de un suelo contaminado por estos compuestos, en una pluma de contaminación.

2.3. La presencia de agente quelante (citrato de sodio y ácido cítrico) en la aplicación de persulfato activado para eliminar biodiesel no supuso una mejora en el proceso, ya que se obtuvieron unos valores de conversión de TPH insignificantes. Los mejores resultados fueron con el uso de nanopartículas de hierro (C_{Fe} = 20 mmol·L^{-1}, C_{PS} = 200 mmol·L^{-1}), donde se

alcanzó una conversión de TPH cercana al 60% en un suelo con 1000 $mg \cdot kg^{-1}$ de TPH de biodiesel B20.

2.4. Dado el carácter recalcitrante de los componentes alifáticos, y del secuestro de radicales sulfato por un exceso de hierro, la adición de 6 dosis sucesivas de nanopartículas (C_{Fe} = 20 $mmol \cdot L^{-1}$) al medio solamente mejoró la eliminación del contaminante de un X_{TPH} ~ 60 % (C_{Fe0} = 20 $mmol \cdot L^{-1}$, C_{PS0} = 200 $mmol \cdot L^{-1}$, C_{TPH0} = 1000 $mg \cdot kg^{-1}$) a un X_{TPH} ~ 62% (C_{Fe} total añadida = 120 $mmol \cdot L^{-1}$, C_{PS0} = 200 $mmol \cdot L^{-1}$, C_{TPH0} = 1000 $mg \cdot kg^{-1}$).

3. **Eliminación de PAHs:**

3.1. El factor controlante en la aplicación del reactivo *Fenton-like* es el tiempo de reacción. En las condiciones más favorables de los tratamientos con sulfato férrico como fuente de hierro (Fe(III)), se consiguieron eliminar cada uno de los PAH prácticamente en su totalidad ($C_{Fe(III)0}$ = 5 $mmol \cdot L^{-1}$, $C_{H_2O_20}$ = 882 $mmol \cdot L^{-1}$), pero la acidificación del medio hasta un pH cercano a 3 y el corto tiempo de tratamiento, donde el oxidante se consumió completamente en 10 días, son dos desventajas importantes a la hora de aplicar esta técnica en un caso real. Sin embargo, en unas condiciones menos severas ($C_{Fe(III)0}$ = 1 $mmol \cdot L^{-1}$, $C_{H_2O_20}$ = 882 $mmol \cdot L^{-1}$), antraceno y benzo(a)pireno se eliminaron prácticamente en su totalidad (X_{ANT} > 99%, X_{BaP} = 95%), fenantreno en un 79% y pireno en un 44%. En estas condiciones, el pH estaba cerca de la neutralidad y la concentración de hierro en disolución durante el tratamiento fue de 0.1 $mmol \cdot L^{-1}$, permitiendo catalizar el peróxido de hidrógeno.

3.2. La adición de un tensioactivo, dodecil sulfato de sodio, facilita la disponibilidad de los contaminantes cara a la reacción de oxidación con peróxido de hidrógeno o persulfato. La presencia de surfactante mejoró sensiblemente las eficiencias de eliminación de los hidrocarburos aromáticos policíclicos con respecto al tratamiento *Fenton-like* por sí solo ($C_{Fe(III)0}$ = 1 $mmol \cdot L^{-1}$, $C_{H_2O_20}$ = 882 $mmol \cdot L^{-1}$), principalmente en las de fenantreno y pireno (X_{PHE} ~ 80%, X_{PYR} ~ 80%). En los tratamientos con persulfato activado, también se observó una sensible mejoría en los experimentos con

persulfato (X_{PHE} ~ 70%) que sin él (X_{PHE} ~ 60%), en unas condiciones similares ($C_{Fe(II)0}$ = 1 mmol·L^{-1}, C_{PS0} = 200 mmol·L^{-1})

3.3. El papel de las partículas de hierro cerovalente como fuente dosificadora de hierro está fuertemente limitado por el pH del medio. En los tratamientos con peróxido de hidrógeno el pH medio fue ligeramente ácido, lo que limitó la solubilidad del hierro en disolución. Aunque se consiguieron eliminar casi completamente antraceno y benzo(a)pireno (X_{ANT} > 99%, X_{BaP} > 99%), las conversiones de fenantreno (X_{PHE} ~ 45%) y de pireno (X_{PYR} ~ 36%) fueron inferiores a las alcanzadas para los mismos contaminantes (X_{PHE} ~ 80%, X_{PYR} ~ 80%) con *Fenton-like* catalizado por Fe(III) en las mismas condiciones (C_{Fe0} = 1 mmol·L^{-1}, $C_{H_2O_20}$ = 882 mmol·L^{-1}).

3.4. El pH ácido del medio fue cercano a 2, favorece la solubilización del hierro en la fase acuosa favoreciendo una activación progresiva del persulfato. Además, la activación progresiva del persulfato con hierro cero-valente minimiza su consumo improductivo y mejora la eficiencia del proceso. Como ya sucedió en el caso del biodiesel B20, la activación con nanopartículas de hierro cerovalente ofreció de nuevo mejores resultados (X_{ANT} ~ 100%, X_{PHE} ~ 100%, X_{PYR} ~ 95% y X_{BaP} ~ 100%) que con activación con Fe(III) (X_{ANT} ~ 100%, X_{PHE} ~ 60%, X_{PYR} ~ 95% y X_{BaP} ~ 100%), en las mismas condiciones iniciales (C_{Fe0} = 1 mmol·L^{-1}, C_{PS0} = 200 mmol·L^{-1}).

3.5. La concentración de los PAHs, así como de persulfato en los distintos tratamientos con persulfato activado se describen con una ecuación cinética de pseudo-primer orden. Dicho modelo cinético obtenido de los datos obtenidos para la oxidación de los PAHs en tratamiento con Fe(III) en discontinuo ha permitido predecir de forma razonada las concentraciones medias de contaminantes y de persulfato a lo largo de una columna en el tratamiento de un suelo contaminado con los mismos PAHs en ensayos llevados a cabo en continuo tras 25 días ($C_{Fe(III)0}$ = 1 mmol·L^{-1}, C_{PS0} = 200 mmol·L^{-1}).

4. **Conclusiones generales:**

4.1. En la aplicación del reactivo Fenton modificado, el citrato de sodio se degrada en productos de oxidación no tóxicos, de los que se han identificado ácido oxálico, málico y 3-oxoglutárico. Además se mineraliza en un 26% en condiciones experimentales de trabajo (C_{CT0} = 50 mmol·L^{-1}, $C_{H_2O_2}$ = 1470 mmol·L^{-1}) que se utilizaron en la eliminación de etilbenceno.

4.2. No se liberaron al medio acuoso especies de mayor potencial tóxico que el etibenceno y el biodiesel B20 tras los tratamientos con reactivo Fenton modificado, utilizando citrato de sodio como agente quelante. Los ensayos de ecotoxicidad por Microtox® de la fase acuosa, basados en la actividad luminiscente de la especie bacteriana *Vibrio fischeri*, antes y después de los tratamientos, mostraron una reducción en la toxicidad de la fase acuosa.

4.3. La solubilidad y oxidabilidad de los contaminantes estudiados son dos factores muy importantes que afectan a la efectividad y tiempo requerido con cada tratamiento. Las especies más fácilmente degradables son el etilbenceno, los ésteres metílicos de ácidos grasos pertenecientes al biodiesel, antraceno y benzo(a)pireno en los PAHs. Además, la mayor solubilidad del etilbenceno favoreció su velocidad de oxidación en fase acuosa. La mayor resistencia a la degradación la mostraron los hidrocarburos alifáticos procedentes del diesel así como fenantreno y pireno.

4.4. El secuestro de radicales cuando el peróxido de hidrógeno se encuentra en exceso da lugar a un consumo improductivo importante que afecta a la eficiencia de los tratamiento. Se apreciaron sensibles aumentos en las conversiones de contaminante con el aumento de la concentración inicial de peróxido de hidrógeno en los diferentes tratamientos, de 1470 mmol·L^{-1} (X_{EB} ~ 50%, $C_{Fe(III)0}$ = 5 mmol·L^{-1}, C_{CT0} = 50 mmol·L^{-1}) a 4410 mmol·L^{-1} (X_{EB} ~ 60%, $C_{Fe(III)0}$ = 5 mmol·L^{-1}, C_{CT0} = 50 mmol·L^{-1}) para la eliminación de etilbenceno (C_{EB0} = 188 mmol·kg^{-1}), de 2000 mmol·L^{-1} (X_{TPH} ~ 70%, $C_{Fe(III)0}$ = 20 mmol·L^{-1}) a 4000 mmol·L^{-1} (X_{TPH} ~ 75%, $C_{Fe(III)0}$ = 20 mmol·L^{-1}) para la eliminación de biodiesel B20 (C_{TPH0} = 1000 mg·kg^{-1}) y de 882 mmol·L^{-1} (X_{ANT} ~ 100%, X_{PHE} ~

80%, X_{PYR} ~ 40%, X_{BaP} ~ 100%, $C_{Fe(III)0}$ = 1 mmol·L^{-1}) a 1765 mmol·L^{-1} (X_{ANT} ~ 100%, X_{PHE} ~ 80%, X_{PYR} ~ 80%, X_{BaP} ~ 100%, $C_{Fe(III)0}$ = 1 mmol·L^{-1}).

4.5. En la eliminación de biodiesel B20 y de hidrocarburos aromáticos policíclicos con persulfato activado, las mejores eficiencias de eliminación se consiguieron cuando la activación fue llevada cabo con la adición de nanopartículas de hierro. La naturaleza de las nanopartículas de hierro cerovalente permiten actuar como una fuente continua de hierro, en la que el hierro cerovalente se oxida primeramente a Fe(II), que es la especie que desencadena la liberación de los radicales sulfato. La activación directa por Fe(II) ofreció resultados inferiores por el secuestro de radicales.

4.6. La presencia de Fe(III) permite activar el persulfato, aunque no directamente, ya que necesita reducirse previamente a Fe(II), bien por la presencia de especies reductoras ya presentes en el medio, o por la acción de compuestos quinónicos, que actúan como especies electrófilas, como es el caso de la 9,10-antracenodiona, originada por la oxidación del antraceno de manera natural o por oxidación química. En los ensayos en continuo, se observó una relación directa a lo largo de la columna entre la concentración de hierro, identificado como Fe(III) lábil y la conversión de cada uno de los PAH.

4.7. Debido al bajo contenido en materia orgánica del suelo tratado y a que los tratamientos no se realizaron sobre un suelo envejecido, el orden de reactividad de los PAHs en el tratamiento con persulfato activado en columna se puede aproximar razonablemente a su correspondiente potencial de ionización, siguiendo el orden BaP (-7.12 eV) > PYR (-7.41 eV) > PHE (-7.86 eV) > ATQ (-9.25).

CONCLUSIONS

From the results obtained regarding the remediation of a contaminated soil with organic, persistent and low water soluble compounds (ethylbenzene, B20 biodiesel blend and PAHs) through the application of chemical oxidation with hydrogen peroxide and persulfate, by adding iron as activator and chelating agent in some cases, the following conclusions are presented:

1. **Ethylbenzene removal:**

   1.1. Since the contaminant degradation occurs in the aqueous phase, ethylbenzene conversion is limited by its water solubility, (C_{EB}^{*}), 180 mg·L^{-1}, and, at the same time it inversely depends on the initial concentration in soil, as shown in Eq. [5.1]

$$X_{EB} = \frac{k \cdot C_{H_2O_2}^{n} \cdot C_{EB}^{*} \cdot t}{C_{EB_0}} \cdot \frac{V_L}{W_s} \qquad [5.1]$$

   1.2. Modified Fenton reagent with tribasic sodium citrate as chelating agent (C_{CT0} = 50 mmol·L^{-1} in the aqueous phase) increases the oxidant lifetime in the media as well as keeps iron in solution at a circumneutral pH. Under the experimental conditions tested, near total conversion of ethylbenzene was reached until 6600 mg·kg^{-1} ehtylbenzene in soil. Nevertheless, for the treatments in which ethylbenzene was present in soil at 20000 mg·kg^{-1}, the maximum conversion reached was near 60% (C_{CT0} = 50 mmol·L^{-1}, $C_{H_2O_20}$ = 4410 mmol·L^{-1}, $C_{Fe(III)0}$ = 5 mmol·L^{-1}).

   1.3. The presence of soil improves the contact between the organic and the aqueous phase. Ethylbenzene oxidation was faster when reaction was carried out in the presence of soil. Nevertheless, no remarkable differences were noticed regarding final ethylbenzene conversion, achieving X_{EB} = 98% (C_{CT0} = 50 mmol·L^{-1}, $C_{Fe(III)0}$ = 27 mmol·L^{-1}, $C_{H_2O_20}$ = 1470 mmol·L^{-1}, N_{EB0} = 0.094 mmol) and X_{EB} = 60% (C_{CT0} = 50 mmol·L^{-1}, $C_{Fe(III)0}$ = 5 mmol·L^{-1}, $C_{H_2O_20}$ = 4410 mmol·L^{-1}, N_{EB0} = 0.94 mmol) after 72 hours treatment of contaminated soil. On the other hand, similar conversions, X_{EB} = 96% and X_{EB} = 59 %,

were obtained after 144 hours when liquid-liquid reactions were performed. Furthermore, the presence of soil involves a high oxidant non-productive consumption, which makes hydrogen peroxide to be degraded faster in the slurry system tan in the liquid-liquid system.

2. **B20 biodiesel removal:**

2.1. As a consequence of the lower solubility of the components of a B20 biodiesel blend (80% aliphatic hydrocarbons and 20% fatty acid methyl esters) compared to ethylbenzene, the maximum contaminant conversion was near 37% under the most favorable experimental conditions (C_{CT0} = 50 mmol·L^{-1}, $C_{Fe(III)0}$ = 20 mmol·L^{-1}, $C_{H_2O_20}$ = 4000 mmol·L^{-1}) during the application of Modified Fenton reagent.

2.2. Regarding B20 biodiesel removal, the best results were obtained when Fenton-like was used (hydrogen peroxide in excess and Fe(III) in form of ferric sulfate). The highest TPH conversion reached was near 75 % for a 1000 mg·kg^{-1} B20 biodiesel-contaminated soil ($C_{Fe(III)0}$ = 20 mmol·L^{-1}, $C_{H_2O_20}$ = 4000 mmol·L^{-1}). Nevertheless, it took about two hours almost up total oxidant consumption (~ 90%). Therefore, despite the high contaminant conversion reached, the lifetime of the oxidant was short, being a drawback for real case applications, where short distances between injection points should be mandatory in order to treat efficiently a contaminant plume under these conditions.

2.3. The presence of chelating agent (sodium citrate and citric acid) during the application of activated persulfate to remove B20 biodiesel did not improve the process, as TPH conversions were negligible. The best results were obtained by adding nanoparticles of zerovalent iron as activator (C_{Fe} = 20 mmol·L^{-1}, C_{PS} = 200 mmol·L^{-1}), where near 60% conversion was achieved for the remediation of a 1000 mg·kg^{-1} B20 biodiesel-contaminated soil.

2.4. Given the recalcitrant nature of the aliphatic compounds in the B20 biodiesel as well as the sulfate radical scavenging effect by the iron excess, the extra addition of 6 consecutive doses of nanoparticles (C_{Fe} = 20 mmol·L^{-1}) to the

media only improved contaminant removal from X_{TPH} ~ 60 % (C_{Fe0} = 20 mmol·L^{-1}, C_{PS0} = 200 mmol·L^{-1}, C_{TPH0} = 1000 mg·kg^{-1}) to X_{TPH} ~ 62%.

3. **PAHs removal:**

3.1. The controlling step during the application of the Fenton-like reagent is the reaction time. Under the most favorable experimental conditions ($C_{Fe(III)0}$ = 5 mmol·L^{-1}, $C_{H_2O_20}$ = 882 mmol·L^{-1}) in the treatments with ferric sulfate as iron source (Fe(III), all PAHs were removed almost totally. However, as well as it was aforementioned, the media acidification (pH around 3) and the short time of treatment, where the oxidant was degraded totally after 10 days treatment, are two important drawbacks to take into account for real case applications. Despite, under less severe conditions ($C_{Fe(III)0}$ = 1 mmol·L^{-1}, $C_{H_2O_20}$ = 882 mmol·L^{-1}), anthracene and benzo(a)pyrene were removed almost totally (X_{ANT} > 99%, X_{BaP} = 95%), phenanthrene conversion was near 79% and pyrene near 44%. In these conditions, pH was slightly acid (pH around 4) and iron concentration in the aqueous phase was not higher than 0.1 mmol·L^{-1}.

3.2. The addition of a surfactant, sodium dodecyl sulfate increased the availability of the contaminants in the aqueous phase, being more degradable for the application of Fenton Reagent or activated persulfate. In this sense, the presence of surfactant in the media slightly improved the PAHs removal efficiencies with respect to the Fenton-like treatment without surfactant addition ($C_{Fe(III)0}$ = 1 mmol·L^{-1}, $C_{H_2O_20}$ = 882 mmol·L^{-1}), mainly regarding phenanthrene and pyrene (X_{PHE} ~ 80%, X_{PYR} ~ 80%). When activated persulfate was combined with surfactant addition, it was also noticed a slight improvement in terms of pyrene removal, obtaining near 70% phenanthrene conversion with surfactant addition and X_{PHE} = 60% without it, under similar initial concentrations of oxidant and activator ($C_{Fe(II)0}$ = 1 mmol·L^{-1}, C_{PS0} = 200 mmol·L^{-1}).

3.3. The role of nanoparticles of zerovalent iron as continuous releasing source is strongly limited by the pH in the media. During the treatments with Fenton-reagent, pH in the media was slightly acid, which limited iron solubilty in the aqueous phase. In these conditions, although anthracene and benzo(a)pyrene

were removed almost totally, phenanthrene and pyrene conversions (X_{PHE} ~ 45%, X_{PYR} ~ 40%) were lower than those reached with Fenton-like by adding Fe(III) as catalyst under the same initial concentration of iron and hydrogen peroxide (C_{Fe0} = 1 mmol·L^{-1}, $C_{H_2O_20}$ = 882 mmol·L^{-1}).

3.4. In case of activated persulfate, an acidic pH (~ 2) was found so iron solubilization was improved, as it was the effect of zerovalent iron as a continuous releasing source of activator. However, as it happened similarly to B20 biodiesel removal, activation with nanoparticles of zerovalent iron gave better results (X_{ANT} ~ 100%, X_{PHE} ~ 100%, X_{PYR} ~ 95% y X_{BaP} ~ 100%) than with Fe(II) activation (X_{ANT} ~ 100%, X_{PHE} ~ 60%, X_{PYR} ~ 95% y X_{BaP} ~ 100%) under the same initial conditions (C_{Fe0} = 1 mmol·L^{-1}, C_{PS0} = 200 mmol·L^{-1}).

3.5. PAHs and persulfate concentrations were predicted accurately according pseudo-first order kinetics. Besides, the kinetic model obtained from batch experiments could predict reasonably the average concentrations of contaminants in column experiments when Fe(III) was used as activator.

4. **General conclusions:**

4.1. Sodium citrate is degraded into non-toxic degradation byproducts during the application of Modified Fenton Reagent, identifying oxalic, malix and 3-oxoglutaric acids. Mineralization of chelating agent was near 26% under the experimental conditions used (C_{CT0} = 50 mmol·L^{-1}, $C_{H_2O_2}$ = 1470 mmol·L^{-1}) for ethylbenzene removal.

4.2. The degradation of ethylbenzene and B20 biodiesel did not result in the release of degradation by products with higher toxicity than the original pollutants. Ecotoxicity assays, based on the luminescence of *Vibrio fischeri,* after the treatments with Modified Fenton Reagent with sodium citrate as chelating agent, showed a decrease in the toxicity of the aqueous phase.

4.3. Solubility and oxidability are key factors for the effectiveness and time required for each treatment. The most degradable species where ethylbenzene, fatty acid methyl esters from B20 biodiesel, anthracene and benzo(a)pyrene. Furthermore,

since ethylbenzene solubility was the highest among all pollutants treated, its oxidation rate in the aqueous phase was the highest as well. However, the highest resistance to degradation was given by aliphatic hydrocarbons, pyrene and phenanthrene.

4.4. There is an important non-productive consumption of hydrogen peroxide when it is added in excess with respect to the stoichiometry value as a consequence of radical scavenging. This fact has a great influence on the effectiveness of the treatment. Slight increase on the contaminant conversions were achieved when hydrogen peroxide initial concentration was increased, from 1470 $mmol \cdot L^{-1}$ (X_{EB} ~ 50%, $C_{Fe(III)0}$ = 5 $mmol \cdot L^{-1}$, C_{CT0} = 50 $mmol \cdot L^{-1}$) to 4410 $mmol \cdot L^{-1}$ (X_{EB} ~ 60%, $C_{Fe(III)0}$ = 5 $mmol \cdot L^{-1}$, C_{CT0} = 50 $mmol \cdot L^{-1}$) for ethylbenzene removal (C_{EB0} = 188 $mmol \cdot kg^{-1}$), from 2000 $mmol \cdot L^{-1}$ (X_{TPH} ~ 70%, $C_{Fe(III)0}$ = 20 $mmol \cdot L^{-1}$) to 4000 $mmol \cdot L^{-1}$ (X_{TPH} ~ 75%, $C_{Fe(III)0}$ = 20 $mmol \cdot L^{-1}$) for B20 biodiesel removal (C_{TPH0} = 1000 $mg \cdot kg^{-1}$) and from 882 $mmol \cdot L^{-1}$ (X_{ANT} ~ 100%, X_{PHE} ~ 80%, X_{PYR} ~ 40%, X_{BaP} ~ 100%, $C_{Fe(III)0}$ = 1 $mmol \cdot L^{-1}$) to 1765 $mmol \cdot L^{-1}$ (X_{ANT} ~ 100%, X_{PHE} ~ 80%, X_{PYR} ~ 80%, X_{BaP} ~ 100%, $C_{Fe(III)0}$ = 1 $mmol \cdot L^{-1}$) for PAHs removal.

4.5. Persulfate activated by nanoparticles of zerovalent iron leaded to the best removal efficiencies achieved for B20 biodiesel and PAHs removal. The nature of nanoparticles of zerovalent iron let this activator release iron to aqueous solution continuosly, being firstly oxidized to Fe(II), which starts the chain reactions for sulfate radicals release. Nevertheless, direct activation by Fe(II) resulted in lower removal efficiencies as a consequence of radical scavenging.

4.6. Persulfate can be activated indirecty by Fe(III) thanks to the presence of reducing species in soils, or by quinolic compounds, which act as electrophilic species, like 9,10-anthrathenedione or anthraquinone, which is an oxidation byproduct of anthracene. In this sense, in the experiments carried out in column, it was found a direct relationship between Fe(III), identified as labile, and PAHs conversion.

4.7. Given the low organic matter content in the soil treated, as well as the fact that the treatments were not carried out on aged soil, PAHs reactivity towards

oxidation with activated persulfate by different sources of iron are tightly related with their oxidation potentials, following the order BaP (-7.12 eV) > PYR (-7.41 eV) > PHE (-7.86 eV) > ATQ (-9.25eV).

6.

NOMENCLATURA/ *ABBREVIATIONS*

EPA	Agencia medioambiental de los Estados Unidos (*Environment Protection Agency*)
EEA	Agencia europea del Medio Ambiente *(Environmental European Agency)*
ISCO	Oxidación Química In Situ (*In Situ CHemical Oxidation*)
Fe(III)	Ión férrico *(Ferric ion)*
Fe(II)	Ión ferroso *(Ferrous ion)*
ZVI	Hierro cero-valente *(zerovalent iron)*
nZVI	Nanopartículas de hierro cerovalente *(nanoparticles of zerovalent iron)*
gZVI	Particulas granulares de hierro cero-valente *(granular particles of zerovalent iron)*
FAME	Ésteres metílicos de ácidos grasos (*Fatty Acid Methyl Esters)*
PAH	Hidrocarburos aromáticos policíclicos *(Polycyclic Aromatic Hydrocarbons)*
SDS	Dodecil sulfato de sodio *(Sodium Dodecyl Sulfate)*
PHE	Fenantreno (*Phenanthrene)*
ANT	Antraceno (*Anthracene)*
PYR	Pireno (*Pyrene)*
BaP	Benzo(a)pireno *(Benzo(a)pyrene)*
ATQ	Antraquinona *(Anthraquinone)*
POP	Contaminantes orgánicos persisntentes (*Persistent Organic Pollutants)*
NOD	Demanda natural de oxidante *(Natural Oxidant Demand)*
BTEX	Benceno, Tolueno, Etilbenceno y Xilenos *(Benzene, Toluene, Ethylbenzene and Xylenes)*
EIONET	Red Europea de Información y Observación del Medio Ambiente *(European Environment Information and Observation Network)*
NAPL	Fases líquidas no acuosas *(Non-aqueous phase liquids)*
DNAPL	Fases líquidas densas no acuosas *(Dense non-aqueous phase liquids)*
LNAPL	Fases líquidas ligerasa no acuosas *(Light non-aqueous phase liquids)*
PCB	Bifenilos policlorados *(Polychlorinated biphenils)*
PCDF	Dibenzo furanos policlorados *(Polychlorinated dibenzofurans)*
TPH	Hidrocarburos totales del petróleo *(Total petroleum hydrocarbons)*
MFR	Reactivo Fenton modificado *(Modified Fenton Reagent)*
PTFE	Politetrafluoroetileno (*Polytetrafluoroethylene)*
SOM	Materia orgánica del suelo *(Soil organic matter)*

TC	Carbonototal en suelo *(Soil total carbon)*
IC	Carbono inorgánico en suelo (*Inorganic carbón in soil)*
EDTA	Ácido etilendiaminotetraacético *(Ethylendiaminetetraacetic acid)*
dp	Diámetro medio de particula de gZVI *(Average particle diameter)*
C_{CT}	Concentración de citrato de sodio en la fase acuosa a un tiempo dado *(Sodium citrate concentration in aqueous solution at a given time)* $mmol \cdot L^{-1}$
C_{CT0}	Concentración inicial de citrato de sodio en la fase acuosa *(Sodium citrate concentration in aqueous phase at the beginning of the treatment)* $mmol \cdot L^{-1}$
X_{CT}	Conversión de citrato de sodio a un tiempo dado (*Sodium citrate conversion at a given time)*
TOC	Carbono orgánico total *(Total organic carbon) %*
TOC_0	Carbono orgánico total inicial en fase acuosa *(Total organic carbón in aqueous phase at the beggining of the treatment) %*
$C_{H_2O_2}$	Concentración de peróxido de hidrógeno en disolución acuosa a un tiempo dado *(Hydrogen peroxide concentración in aqueous phase at a given time)* $mmol \cdot L^{-1}$
$C_{H_2O_20}$	Concentración inicial de peroxido de hidrógeno en la fase acuosa *(Hydrogen peroxide concentration in aqueous phase at the beginning of the treatment)* $mmol \cdot L^{-1}$
C_{EB}	Concentración de etilbenceno en suelo a un tiempo dado *(Ethylbenzene concentration in soil at a given time)* $mmol \cdot kg^{-1}$
C_{EB0}	Concentración inicial de etilbenceno en el suelo *(Ethylbenzene concentration in soil at the beginning of the treatment)* $mol \cdot kg^{-1}$
C_{EB}^{*}	Solubilidad de etilbenceno en fase acuosa *(Ethylbenzene solubility in aqueous phase)* $mmol \cdot L^{-1}$
$C_{Fe(III)}$	Concentración de ión férrico en fase acuosa a un tiempo dado *(Ferric ion concetration in aqueous phase at a given time)* $mmol \cdot L^{-1}$
$C_{Fe(III)0}$	Concentracion inicial de ión férrico en fase acuosa *(Ferric ion concentración at the beginning of the treatment)* $mmol \cdot L^{-1}$
$C_{Fe(}$	Concentración de hierro en fase acuosa a un tiempo dado *(Iron concetration in aqueous phase at a given time)* $mmol \cdot L^{-1}$
C_{Fe0}	Concentracion inicial de hierro en fase acuosa *(iron concentración at the beginning of the treatment)* $mmol \cdot L^{-1}$

TU	Unidades de toxicidad de la fase acuosa *(Toxicity uinits of the aqueous phase)*
EC_{50}	Concentración nominal efectiva de inhibición del 50% (*Half maximal effective concentration)* $g \cdot L^{-1}$
X_{EB}	Conversión de etilbenceno a un tiempo dado (*Ethylbenzene conversion at a given time)*
N_{EB}	Moles de etilbenceno *(Ethylbenzene mol)*
N_{EB0}	Moles iniciales de etilbenceno
k_{EB}	Constante cinética de desaparición de etilbenceno *(Ehtylbenzene removal kinetic constant)*
C_{TPH}	Concentración de hidrocarburos totales en el suelo a un tiempo dado *(Total petroleum hydrocabons concentration at a given time)* $mg \cdot kg^{-1}$
C_{TPH0}	Concentración inicial de hidrocarburos totales en el suelo *(Total petroleum hydrocabons concentration at the beginning of the treatment)* $mg \cdot kg^{-1}$
X_{TPH}	Conversión de TPH a un tiempo dado *(TPH conversion at a given time)*
C_{PAH}	Concentación de PAH en el suelo a un tiempo dado *(PAH concentration in soil at a given time),* $mg \cdot kg^{-1}$
C_{PAH0}	Concentración inicial de PAH en el suelo *(PAHS concentración in soil at the beginning of the treatment)* $mg \cdot kg^{-1}$
X_{PAH}	Conversión de -PAH, PHE,ANT,PYR o BaP- a un tiempo dado *(PAH conversión –PHE, ANT, PYR or BaP- at a given time)*
C_{PS}	Concentración de persulfato en fase acuosa a un tiempo dado *(Persulfate concentration in aqueous phase at a given time),* $mmol \cdot L^{-1}$
C_{PS0}	Concentración inicial de persulfato en fase acuosa *(Persulfate concentration in aqueous phase at the beginning of the treatment),* $mmol \cdot L^{-1}$
C_{nZVI}	Concentración de nZVI en fase acuosa a un tiempo dado *(nZVI concentration in aqueous phase at a given time),* $mmol \cdot L^{-1}$
C_{SDS}	Concentración de dodecil sulfato de sodio en fase acuosa a un tiempo dado *(Sodium dodecil sulfate concentration in aqueous phase at a given time),* $mmol \cdot L^{-1}$
C_{SDS0}	Concentración inicial de dodecil sulfato de sodio en fase acuosa *(Sodium dodecil sulfate concentration at the beginning of the treatment),* $mmol \cdot L^{-1}$
V_L	Volumen de fase líquida para experimentos en batch *(Aqueous phase for batch experiments), mL*

W_S	Masa de suelo tratada en los experimentos en batch *(Soil weight for batch experiments), g*
k	Constante cinética intrínseca *(Intrinsic rate constant)*
k_{obs}/k_w	Constante cinética aparente/observada (*Observed/apparent rate constant,)* dia^{-1}
u_i	Velocidad linear del fluido a la entrada de la columna *(Linear velocity at the column entrance), cm·dia*$^{-1}$
ε	Porosidad del suelo *(Soil porosity)*
L	Longitud del suelo dentro de la columna *(Lenght of soil in column), cm*
ρ_L	Densidad aparente del suelo en la columna *(Bulk density of soil in column),* $g \cdot cm^{-3}$

7.

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Anexo I / *Annex I*

Difusión de la investigación:

Contribuciones a Congresos Nacionales e Internacionales

9th European Congress of Chemical Engineering (ECCE13).
La Haya, Holanda.
21-25 abril de 2013

F. Pardo, A. Santos y A. Romero.

REMEDIATION OF HYDROCARBON CONTAMINATED SOILS BY MODIFIED FENTON PROCESS.

Tipo de participación: Póster.

XXXIV Reunión Bienal de la Real Sociedad Española de Química (Santander).
Santander, España
15-18 Septiembre 2013

F. Pardo, A. Santos y A. Romero.

APLICACIÓN DEL REACTIVO FENTON MODIFICADO EN LA REMEDIACIÓN DE SUELOS CONTAMINADOS CON HIDROCARBUROS.

Tipo de participación: Ponencia.

J. M. Rosas, F. Vicente, **F. Pardo**, A. Santos y A. Romero.

REMEDIACIÓN DE SUELOS CONTAMINADOS CON HERBICIDAS MEDIANTE FENTON MODIFICADO.

Tipo de participación: Póster.

3rd European Conference on Environmental applications of Advanced Oxidation Processes.
Almería, España.
27-30 octubre de 2013

F. Pardo y A. Santos.

REMEDIATION OF A DIESEL CONTAMINATED SOIL BY USING A MODIFIED FENTON PROCESS.

Tipo de participación: Póster.

13th Mediterranean Congress of Chemical Engineering
Barcelona, España.
30 septiembre-3 octubre de 2014

F. Pardo, J.M. Rosas, A. Santos y A. Romero

USE OF ACTIVATED PERSULFATE FOR THE REMEDIATION OF A BIODIESEL-BLEND CONTAMINATED SOIL.

Tipo de participación: Póster.

F. Pardo, A. Santos y A. Romero

REMEDIATION OF A PAH-CONTAMINATED SOIL BY OXIDATION WITH FENTON REAGENT AND SIMULTANEOUS SOLUBILIZATION WITH SURFACTANTS.

Tipo de participación: Póster

Aquaconsoil 2015. 13th International UFZ-Deltares Conference on Sustainable Use
Copenhagen, Dinamarca
9-12 junio de 2015

F. Pardo, M. Peluffo, A. Santos y A. Romero

USE OF DIFFERENT KINDS OF PERSULFATE ACTIVATION WITH IRON FOR THE REMEDIATION OF A PAH-CONTAMINATED SOIL.

Tipo de participación: Ponencia.

META2016. XII Reunión de la Mesa Española de Tratamiento de Aguas
Madrid, España
20-22 junio de 2016

F. Pardo, A. Santos y A. Romero

ESTUDIO EN COLUMNA SOBRE LA REMEDIACIÓN DE UN SUELO CONTAMINADO CON PAHS USANDO PERSULFATO ACTIVADO.

Tipo de participación: Póster.